BITMAPS FINDINGS & EXPERIMENTAL RESULTS

"Pilot technology for aerobic Biodegradation of spent TMAH Photoresist solution in Semiconductor industries"

Guglielmo Iuliano Principal EHSS Eng (BITMAPs coordinator)

Francesco Veglio Professor at UNIVAQ (BITMAPs chief scientific officer)

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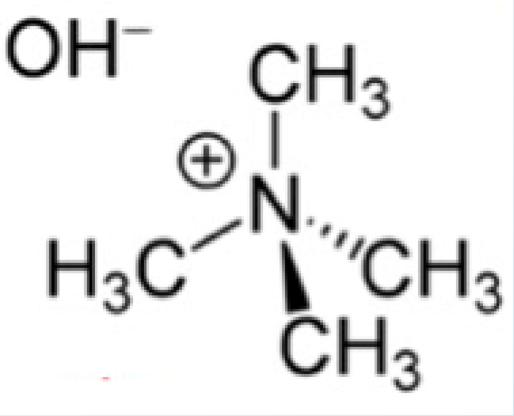
PROJECT FRAMEWORK

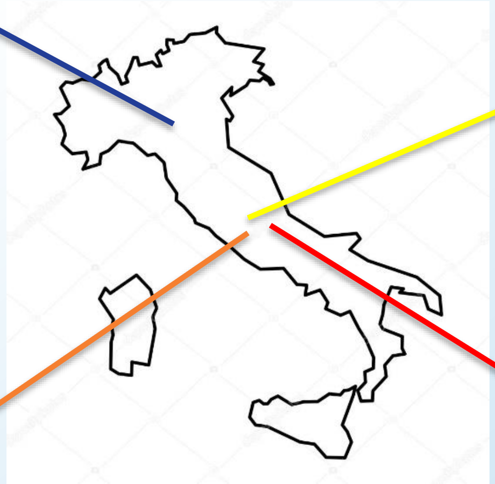


- No armonized classification provided for TMAH
- TMAH dangerousness for humans as well as its ecotoxicity well known in the literature.
- TMAH not regulated in terms of concentration limit by the national environmental law.
- ISS (Istituto Superiore Sanita`) recommended to target 0.4 mg/l in the sewerage and 0.2 mg/l in water bodies in order to comply with EU Water Framework Directive 2000/60/EC.
- Huge costs for LFoundry (coordinating beneficiary of BITMAPS consortium) as the wastewater containing TMAH is currently concentrated on site and then disposed to external authorized plants

BITMAPS CONSORTIUM

B.F.C. Sistemi S.r.l.

UNIVERSITÀ
DEGLI STUDI
DE L'AQUILA



LFOUNDRY
Solutions
for great visions
A SMIC COMPANY

BME Biomaterials & Engineering Srl

KEY OBJECTIVES

- Design, construction and validation of a semi-industrial pilot plant enabling the treatment of spent photoresist-tetramethylammonium hydroxide (PR/TMAH), and other mixed solutions (ammonium fluoride and acid mix internally named "SEZ") generated by the semiconductor manufacturing processes.

- Demonstrate, at industrial scale, the feasibility/sustainability for TMAH treatment through an aerobic biodegradation of such toxic substance carried out by adapted microorganisms selected during the R&D phase.

- Prove the cost sustainability of the process, in a LCC perspective, also taking into account the actual annual operating costs for the disposal of concentrated TMAH and the other waste solutions.

- Pave the way for replication and transfer of the results to E&S Sector.

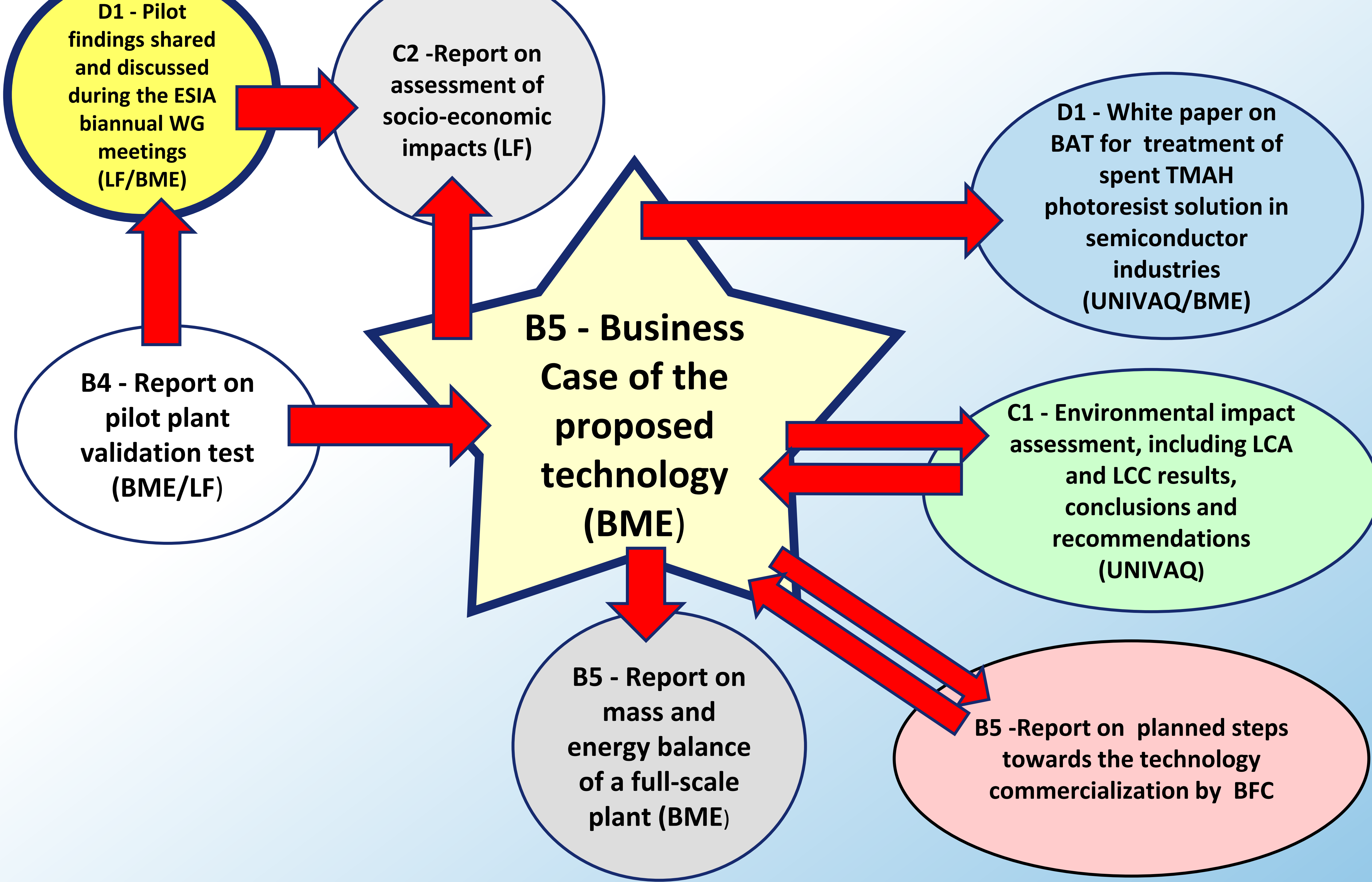
- Propose new quality standards for wastewater discharged helping policy-makers to fill the regulatory gaps on TMAH emissions

THE PILOT PLANT

- The treatment sections of the plant assembled inside two aligned containers (30 ft. each placed on a concrete and chemical proof platform to prevent any possible subsoil contamination in case of leakages) and connected with an external scrubber for the abatement of air emissions.
- TMAH directly fed from the site collecting tank of that waste, whereas ammonium fluoride and acid mix wastewaters are automatically transferred by the operator from drums inside the dedicated section of the plant.
- The first container includes the biological section made by three reactors operating in sequence to accelerate the TMAH degradation. This section can be operated for a wide range of TMAH input flows.
- The other container hosts a chemical-physical section including a reactor and a small filter-press.
- All the volatile substances generated with treatments are captured and conveyed to the scrubber in order to minimize air emissions.
- The output liquid streams from the two treatment sections are collected and discharged to the site biological wastewater treatment plant.

BITMAPS STATUS - NEXT DELIVERABLES

Project duration: Jun 2016 – Dec 2019



RELEVANT INFO

- BITMAPS website: http://www.lifebitmaps.eu/

- BITMAPS “Open Day” likely June 2019 (date to be communicated)

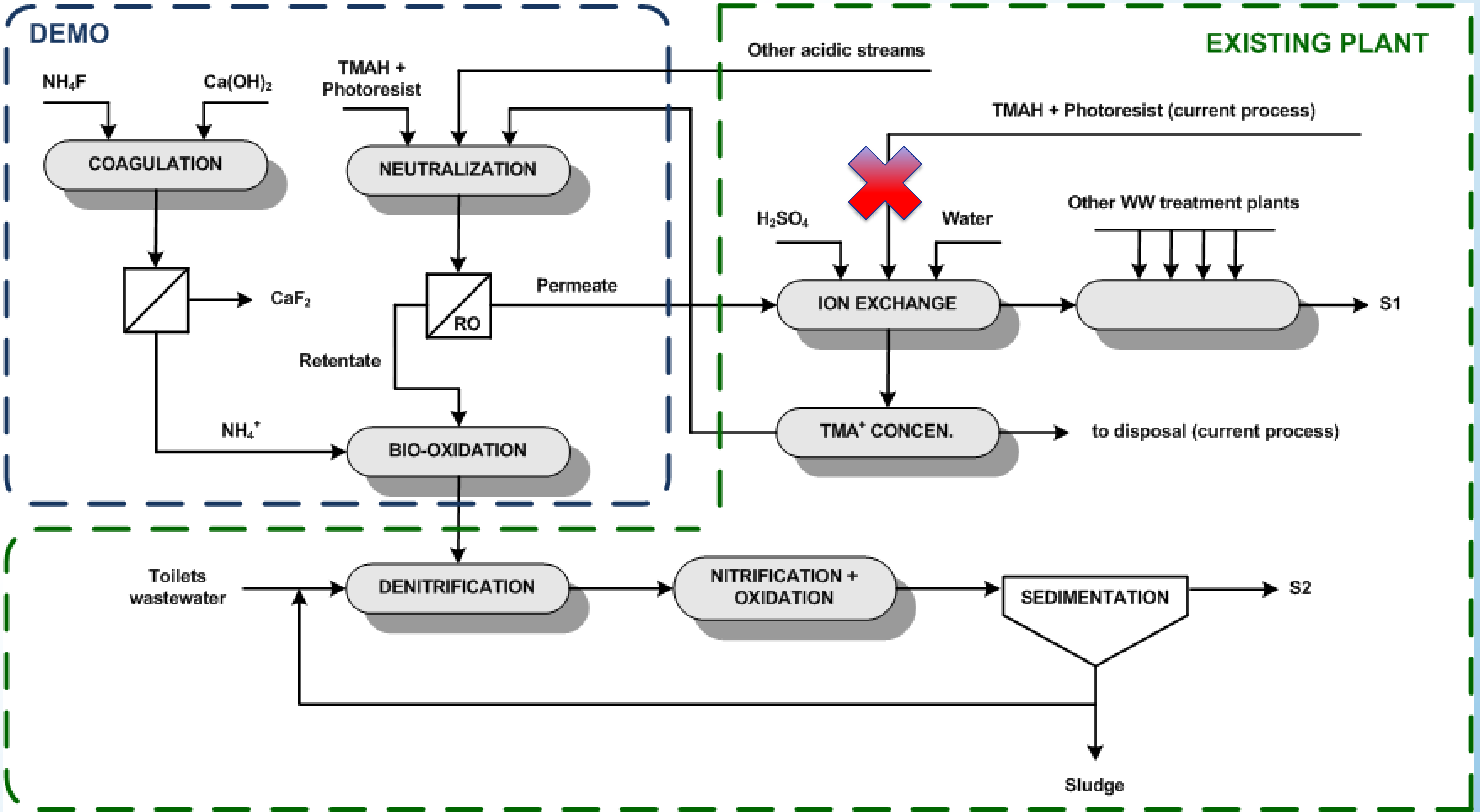
- SURVEY distributed to Semiconductors companies for preliminary information to be used to predict socio-economic impacts :
  - Interest to receive information and updates about the project (Results, Newsletters, events..) ? Y/N
  - presence at their sites of wastewaters containing substances treated by BITMAPS (Y/N)
  - number of affected sites
  - willingness to be contacted by the commercial beneficiaries of BITMAPS to explore the opportunity to implement results at their sites (upon signing a Non-Disclosure Agreement) (Y/N)
  - Company contact names

PROJECT TECHNICAL RESULTS

OUTLINES

1. Preliminar research activity before LIFE BITMAPS
2. Design and construction of pilot plant
3. Experimental results of biooxidation of TMAH
4. Experimental results of chemical precipitation (SEZ, BoE)
5. Process analysis and Industrial Plant Design
6. Preliminary Economical Analysis and LCA

General idea of the project LIFE BITMAPS



General idea of the project LIFE BITMAPS: RO

The study was performed on pilot plant composed by **ultrafiltration (UF) and reverse osmosis (RO) modules** installed in series. due to the membrane characteristics of , a feed neutralization was necessary, two neutralizing agents were tested: **acetic acid and sulfuric.**

The efficiency of removal of TMAH (**initial concentration 1,7 g/L**) was evaluated comparing its inlet concentration to pilot plant with its concentration in permeate comes from RO by acetic acid, the average value was **94.36%** (**88 mg/L** in permeate of RO) , by sulfuric acid reaches **98.81%** (**20 mg/L** in permeate of RO). Final concentration in the retentate of TMAH: **20 g/L**

Fig.2.2.1.3.2. Impianto pilota installato nel parco industriale.

Fig. 2.2.2.3.3. Filtri a cartucce dell'impianto pilota dopo 13 giorni di utilizzo di acido acetico come agente neutralizzante. Nell'ultima illustrazione, parallelo con filtro nuovo.

Mechanism of biodegradation of TMAH

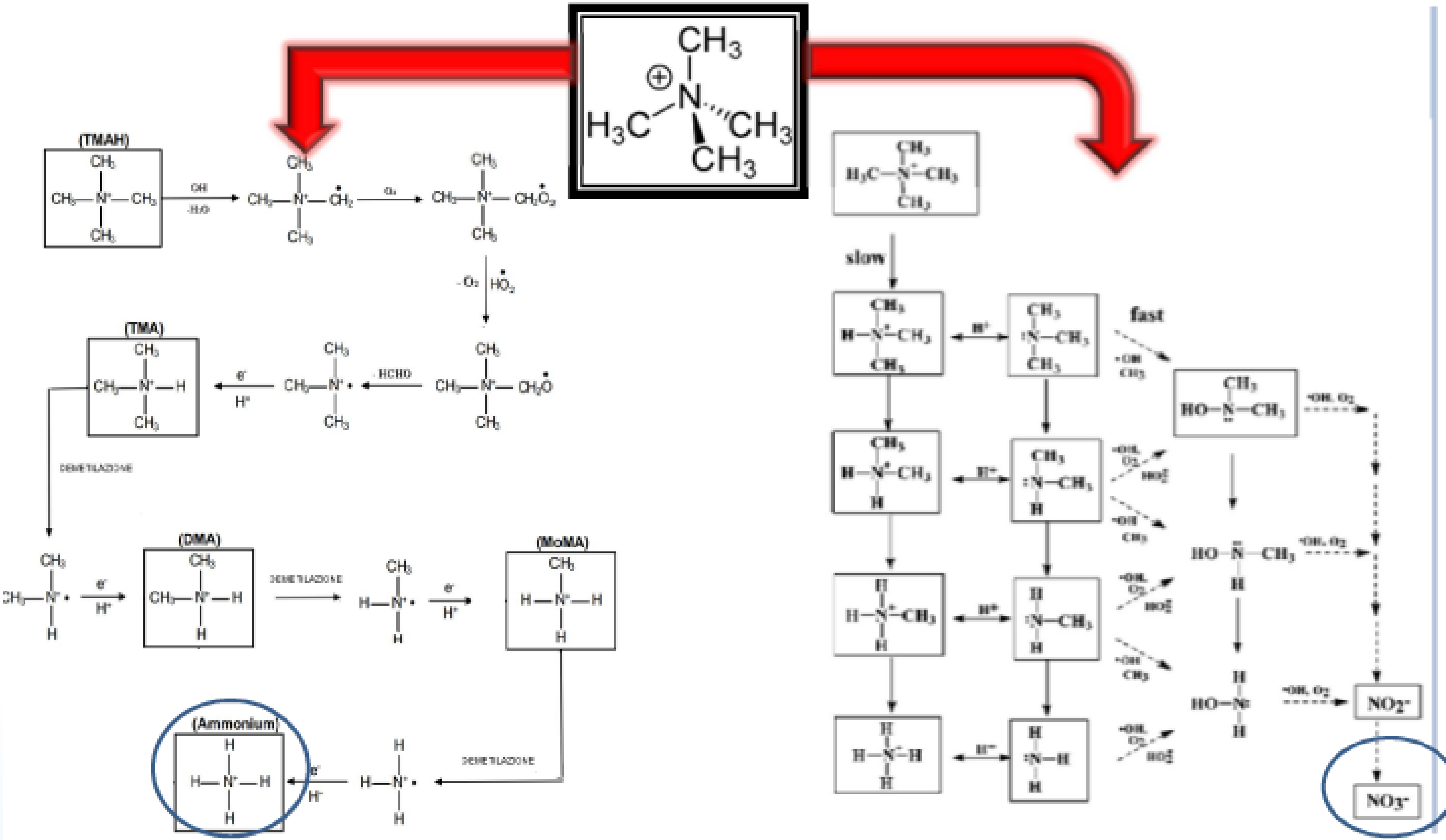
Oxygen Uptake Rate (OUR) and Specific Oxygen Uptake Rate (SOUR)

Sample	OURs endogenous/OURs sample	Note
TMAH as is	0.82	Need further studies
TMAH as is + PR	0.49	Easily biodegraded
TMAH neutralized by AC acid	0.48	Easily biodegraded
TMAH + PR neutralized by AC acid	0.54	Biodegradable

Ratio between OURs endogen/OURs samples (AC = acetic acid; PR = Photoresist)

Demonstration of biodegradation of TMAH in diluted conditions and in presence of other organic compounds

Mechanism of biodegradation of TMAH



Previous work before LIFE BITMAPS

Biological tests carried out in a lab-scale bioreactor: TMAH degradation

Previous work before LIFE BITMAPS

Mathematical modelling of the stoichiometry and kinetic of TMAH biodegradation: analysis of lab-scale bioreactor tests

Stechiometria:

Lo smaltimento del TMAH avviene per mezzo di una selezionata massa batterica ($CH_{1,7}O_{0,45}N_{0,17}$) e produce NH_3, CO_2, H_2O ed altra massa batterica secondo la reazione

$$\text{Substrato} + O_2 \longrightarrow \text{Cellule} + \text{Prodotti}$$

$$\underbrace{C_4H_{12}N}_{\text{TMAH}} + a\underbrace{C_4H_{10}O_2}_{\text{Photoresist}} + bO_2 \longrightarrow c\underbrace{CH_{1.7}O_{0.45}N_{0,2}}_{\text{Biomassa}} + dNH_3 + eCO_2 + fH_2O$$

$$C_4H_{12}N + 4\,C_4H_{10}O_2 + 26{,}413\,O_2 \rightarrow 1{,}75\,CH_{1,7}O_{0,45}N_{0,17} + 0{,}65\,NH_3 + 18{,}25\,CO_2 + 26{,}413\,H_2O$$

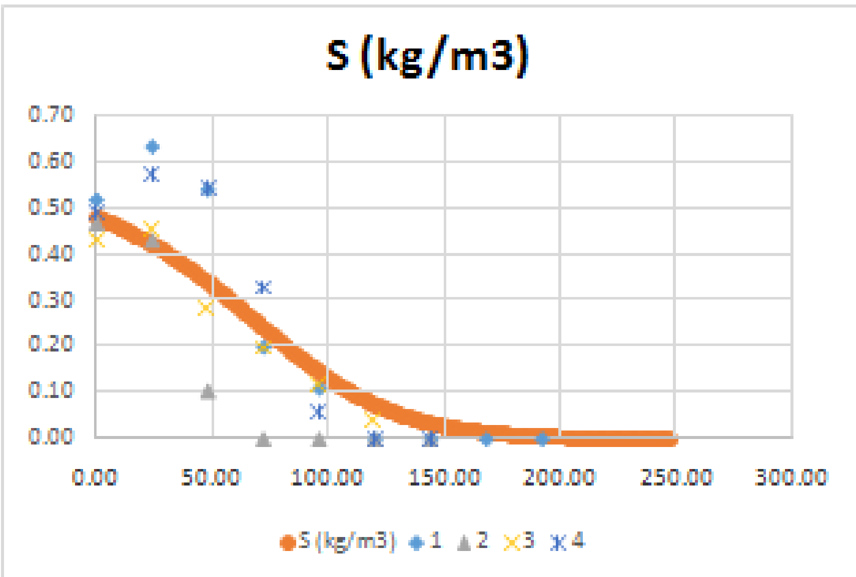
Studio cinetico:

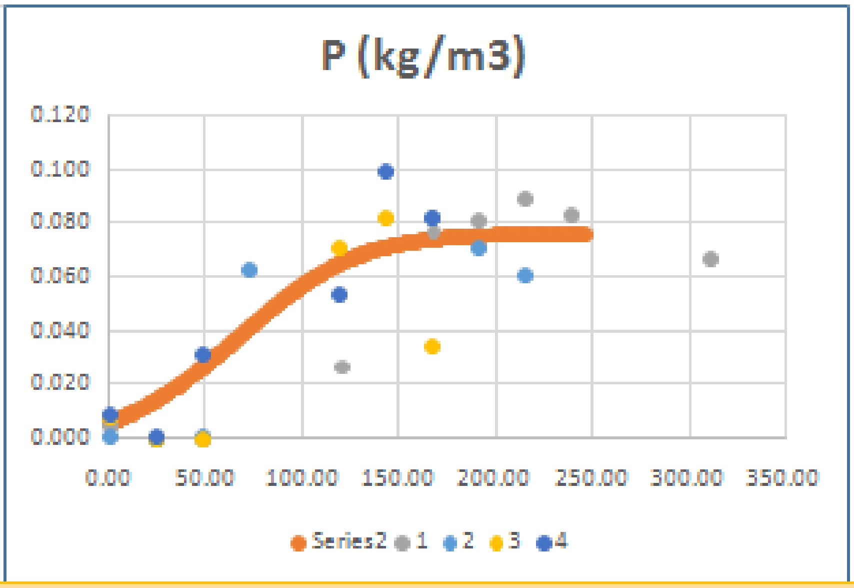
$$\begin{cases} \dfrac{dX}{dt} = \mu \cdot X & t = 0, \quad X = X_0 \\ \dfrac{dS}{dt} = -\sigma \cdot X & t = 0, \quad S = S_0 \\ \dfrac{dP}{dt} = -\sigma \cdot X & t = 0, \quad P = P_0 \\ \mu = \mu_{MAX} \cdot \dfrac{S}{K_S + S} \\ \sigma = \dfrac{1}{Y^G_{X/S}} \cdot \mu + m \\ \pi = \alpha \cdot \mu + \beta \end{cases}$$

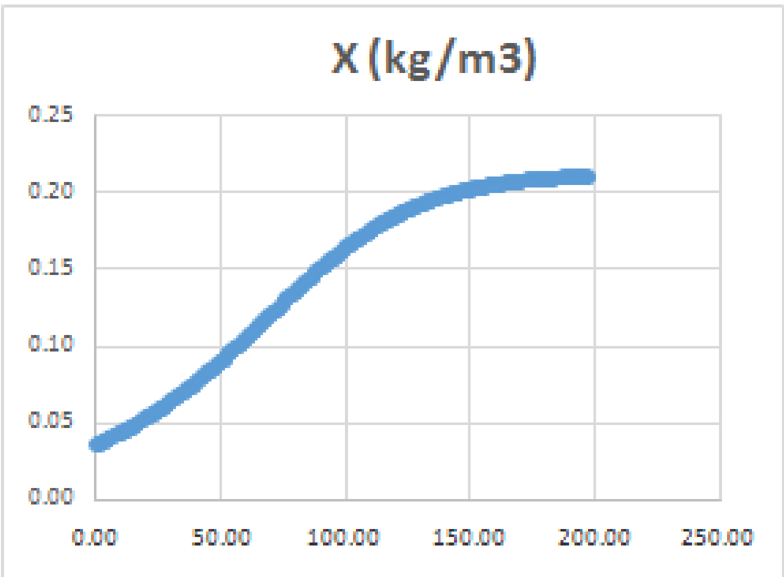
$$\frac{Y^G_{X/S} \cdot K_S + Y^G_{X/S} \cdot S_0 + X_0}{\mu_{MAX} \cdot \left(Y^G_{X/S} \cdot S_0 + X_0\right)} \ln\left[1 + \frac{Y^G_{X/S} \cdot (S_0 - S)}{X_0}\right] - \frac{Y^G_{X/S} \cdot K_S}{\mu_{MAX} \cdot \left(Y^G_{X/S} \cdot S_0 + X_0\right)} \ln\left(\frac{S}{S_0}\right) = t$$

Previous work before LIFE BITMAPS

Experimental results of biodegradation tests in lab-scale and mathematical modelling
(S = TMAH; O = NH4+; X = biomass concentration)





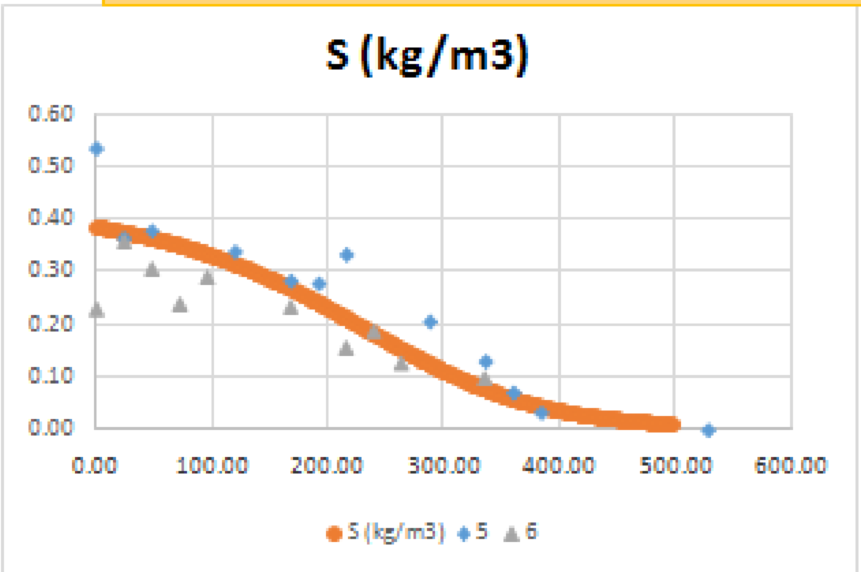


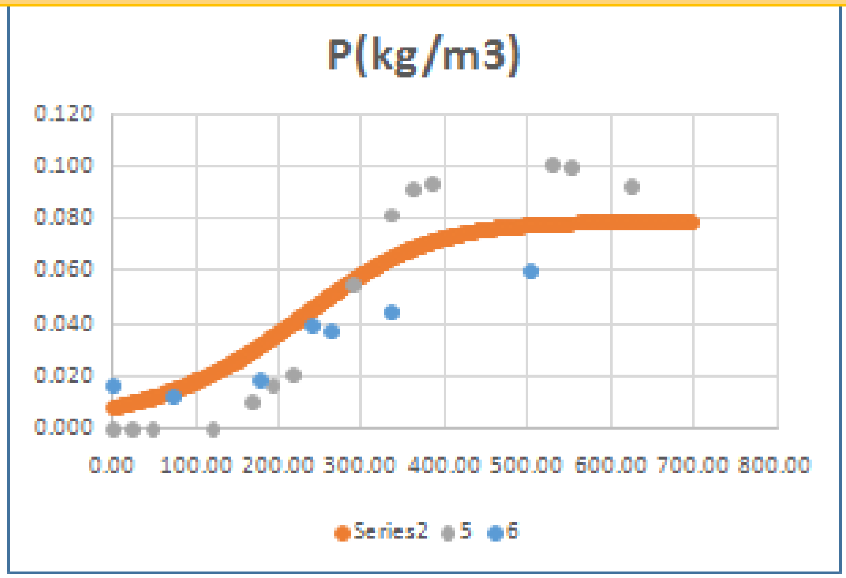
Parametri cinetici ottenuti:

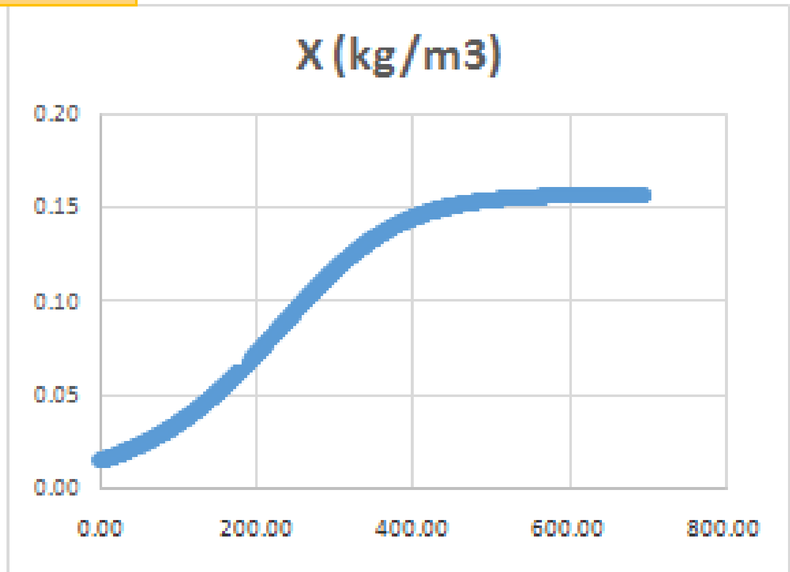
mmax	0,043	h-1
ks	0,8	g/L
yx/s	0,37	g/g

con:

S0	0,431	g/L
X0	0,025	g/L







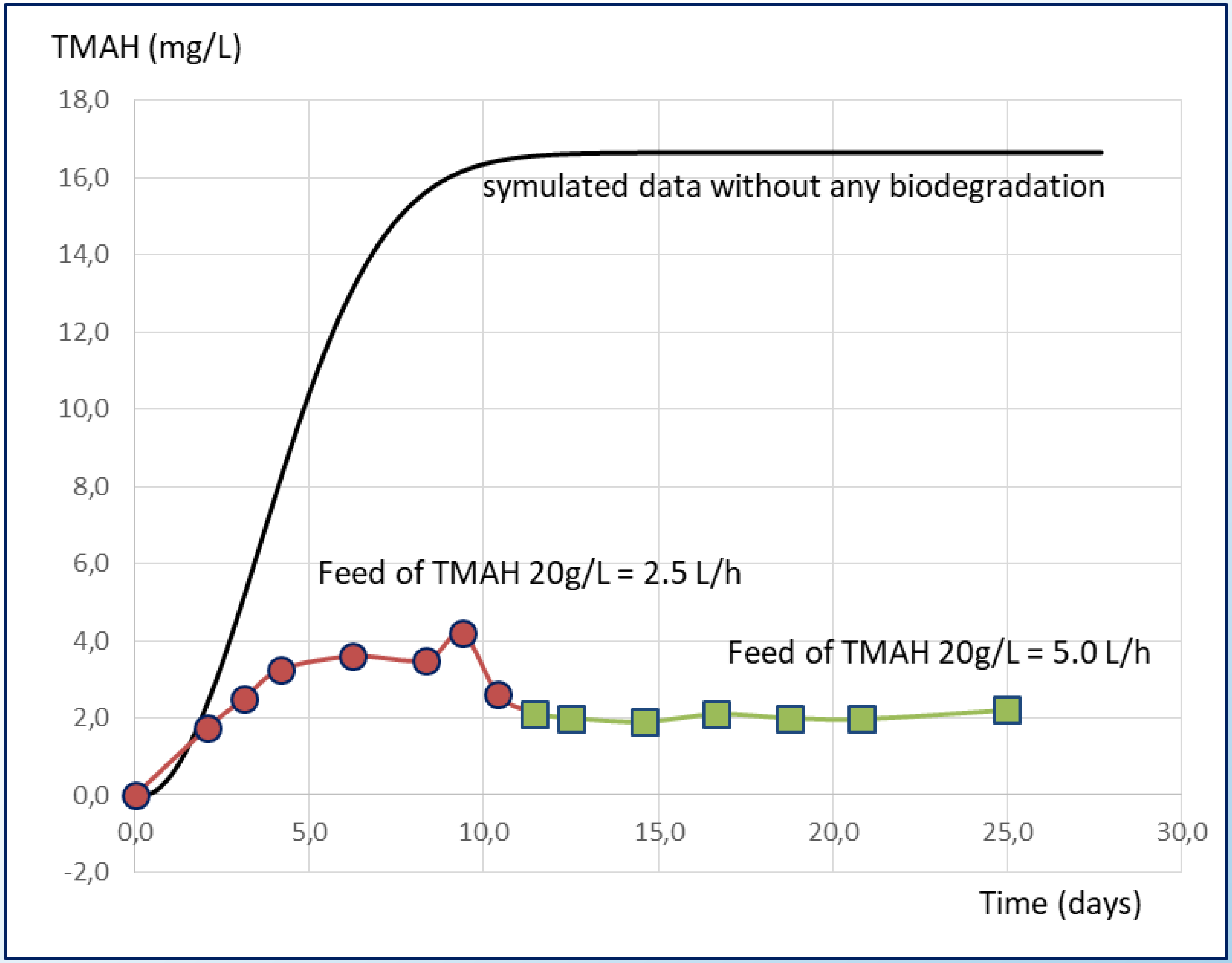
Previous work before LIFE BITMAPS

Study of microbial population of the active sludge biomass after TMAH treatment

Genus/Family	Representative OTU	Features
Comamonas	Comamonas granuli	grows on solvents
	Comamonas nitrativorans	denitrifier
Pseudomonas	Pseudomonas knackmussii strain B13	grows on polyamines
	Pseudomonas nitritireducens	can reduce nitrate
Stenotrophomonas	Stenotrophomonas humii	can reduce nitrate/nitrite
Brevundimonas	B. Abyssalis / Brevundimonas viscosa	nitrate reduction - grow on tween
Sphingomonadaceae	N.A	
Sphingobacteriaceae	N.A	
Methylophilaceae	Methylobacillus glycogenes	grows on methanol and methylamines
Xanthobacteraceae	Methylobrevis pamukkalensis	grows on methanol and methylamines
Xanthobacter	Xantobacter autotrophicus	Methilotroph, Bioremediation of clorinated compounds
Rhodococcus	N.A	

Previous work before LIFE BITMAPS

Retentate was fed to the WWT (active sludge process): in the figure the experimental results in terms of TMAH at the exit of WWT is compared with symulated data (CSTR model without biochemical reaction).



Previous work before LIFE BITMAPS

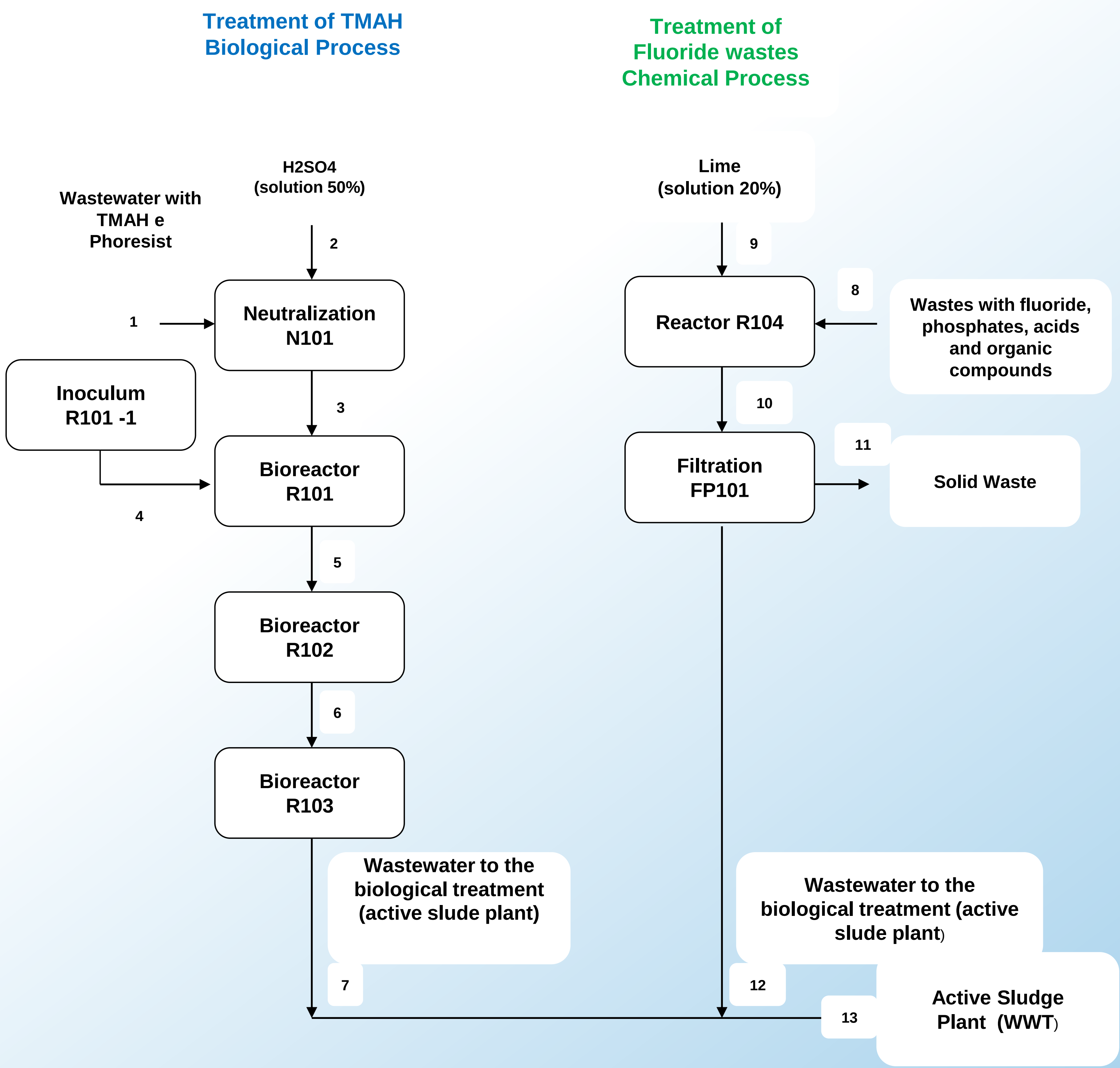
Conclusions of the tests before LIFE BITMAPS:

1. **TMAH can be concentrate with a membrane process (UF+RO) in order to reduce its volume;**
2. **TMAH can be biodegraded after biomass adaptation: stoichiometry and kinetic model identified;**
3. **The biodegradation produce NH4+ as a by-product (without nitrification);**
4. **The concentrate of RO can be fed to a standard WWT but with a low flowrate;**
5. **The kinetic model gives indication that bioreactors in series is a suitable solution to reduce the volumes of bioreactors;**

THIS PROCESS SOLUTION HAS BEEN SELECTED TO REALIZE THE PILOT PLANT

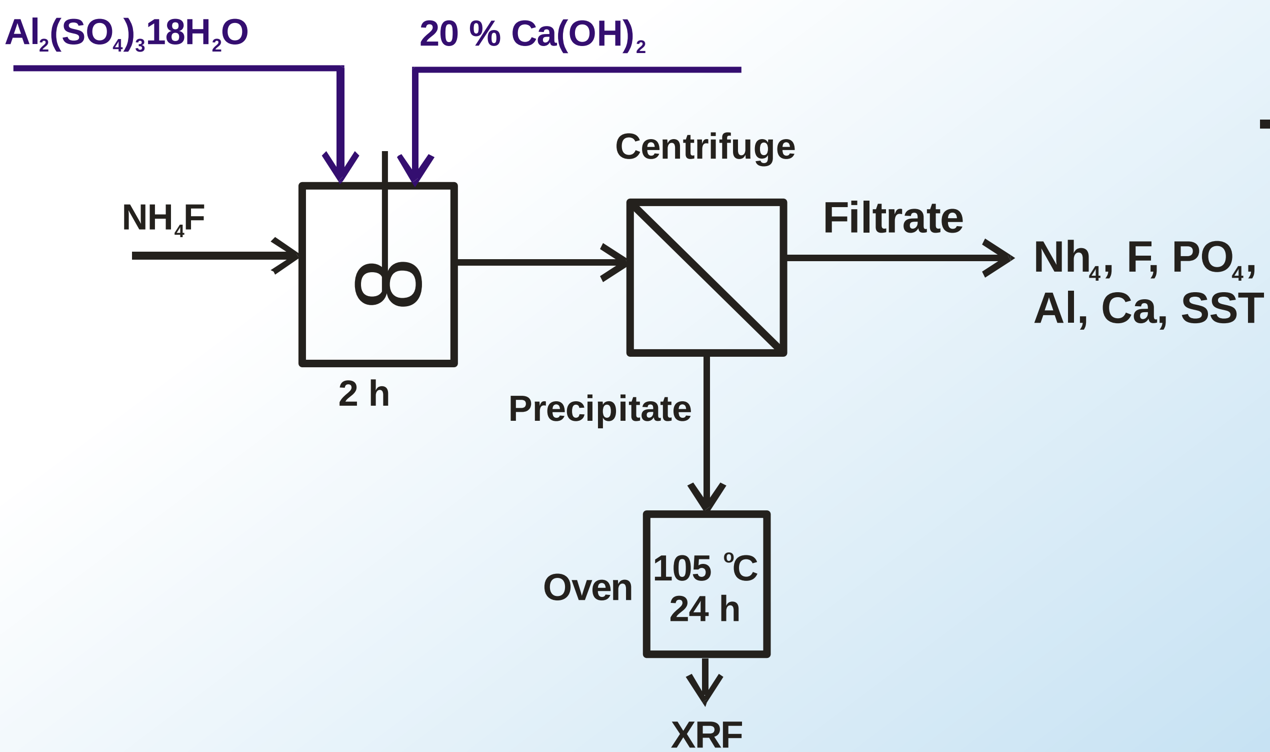
LIFE BITMAPS: block diagram

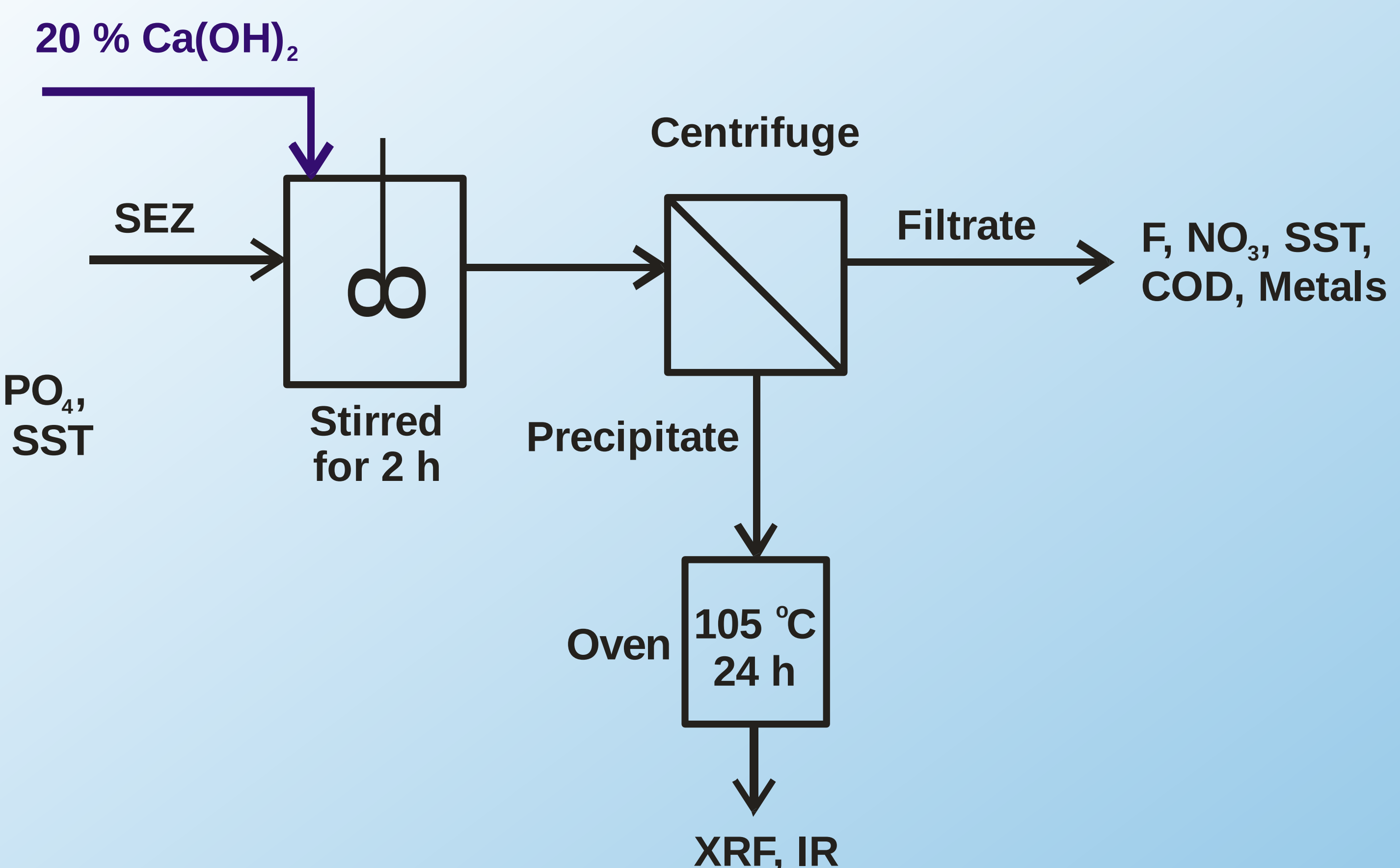
PROCESS FLOWSHEET



Chemical composition of BoE and SEZ

Wastewater	pH	Si, mg/L	F^-, mg/L	PO_4^{3-}, mg/L	NH_4^-, mg/L	NO_3, mg/L	COD, mg/L	CH_3COOH, mg/L	Anionic surfactants, mg/L
NH4F-BoE	8.75	23.5	20,100	1,450	25,700	977	500	-	0
SEZ	1.6	314	16,861	-	-	119,048	109,000	26,112	23.8





LIFE BITMAPS: chemical precipitation BoE-SEZ

Chemical reactions of BoE and SEZ

BoE

$6\ Al_2(SO_4)_3\ (18\ H_2O) + 9\ Ca(OH)_2 \rightarrow\ 18\ \mathbf{Ca_2(SO_4)_3}\downarrow + 4\ Al(OH)_2$

$2\ HNO_3 + Ca(OH)_2 \rightarrow Ca(NO_3)_2 + 2\ H_2O$

$2\ NH_4F + Ca(OH)_2 \rightarrow \mathbf{CaF_2}\downarrow + 2\ NH_4OH$

$NH_4OH \rightarrow NH_3 + H_2O$

$2\ H_3PO_4 + 3\ Ca(OH)_2 \rightarrow Ca_3(PO_4)_2 \downarrow + 6\ H_2O$

SEZ

$2\ HNO_3 + Ca(OH)_2 \rightarrow Ca(NO_3)_2 + 2\ H_2O$

$2\ HF + Ca(OH)_2 \rightarrow \mathbf{CaF_2}\downarrow + 2\ H_2O$

$2CH_3COOH + Ca(OH)_2 \rightarrow Ca(CH_3COO)_2 + 2H_2O$

LIFE BITMAPS: chemical precipitation BoE-SEZ

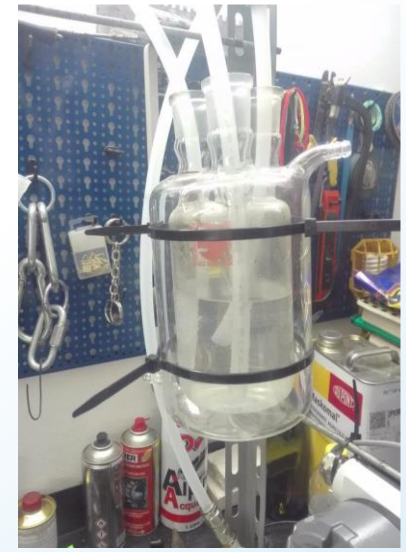
Chemical composition of wastewater after treatment

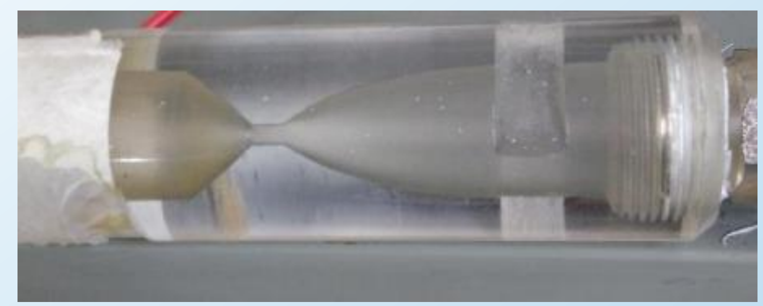
Wastewater	pH	Si, mg/L	F^-, mg/L	PO_4^{3-}, mg/L	NH_4^-, mg/L	NO_3, mg/L	COD, mg/L	CH_3COOH, mg/L	Anionic surfactants, mg/L
NH_4F	11	0.4	8	0	13,300	977	100	-	0
SEZ	4.7	0.4	11	0	-	119,048	73,400	26,112	14.0

Consumption of reagents (to be optimized)

Wastewater	$Al_2(SO_4)_3$ kg/m^3	$Ca(OH)_2$ 20% kg/m^3
NH4F	40	364
SEZ	0	580

LIFE BITMAPS: Hydrocavitation

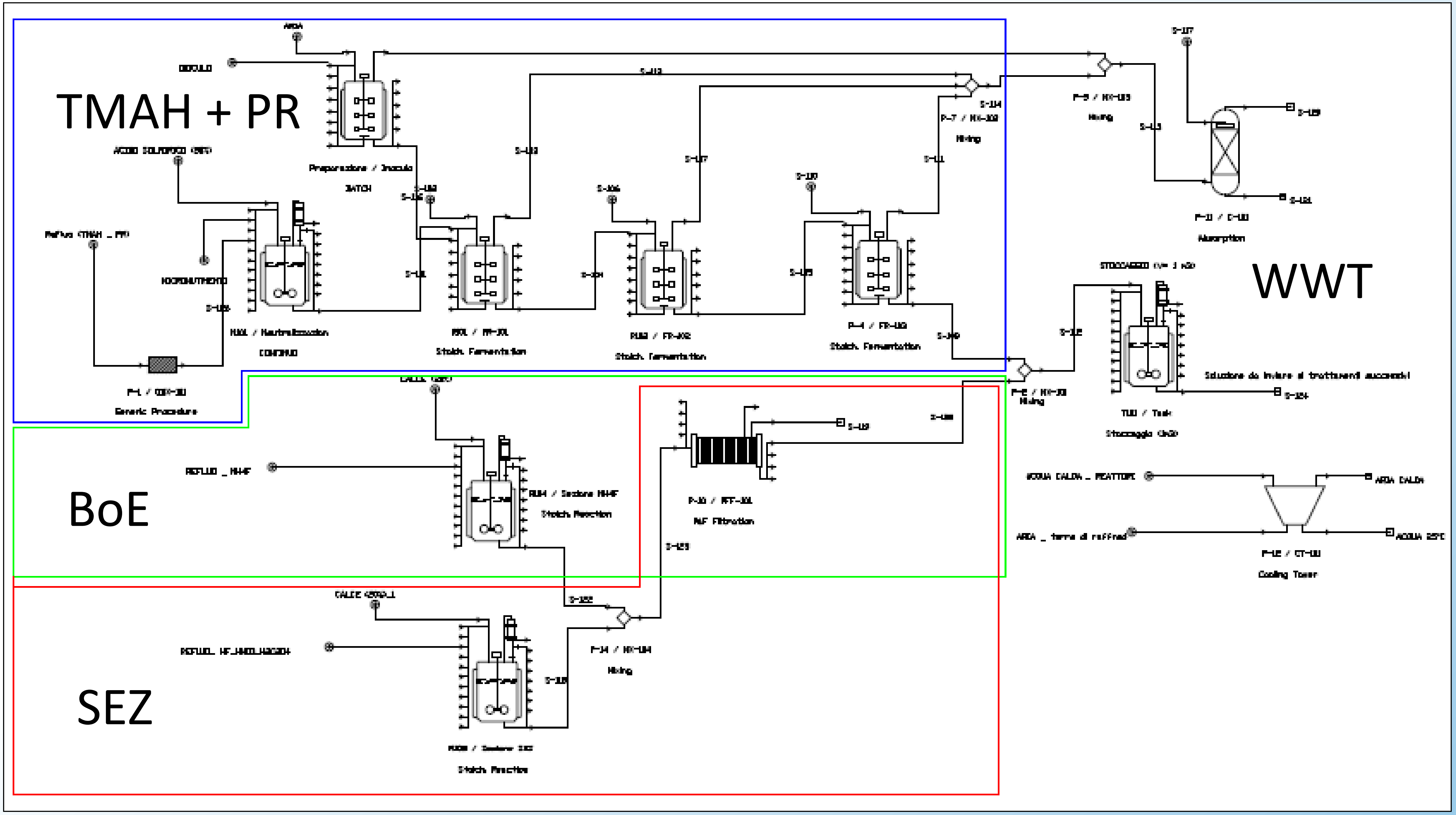




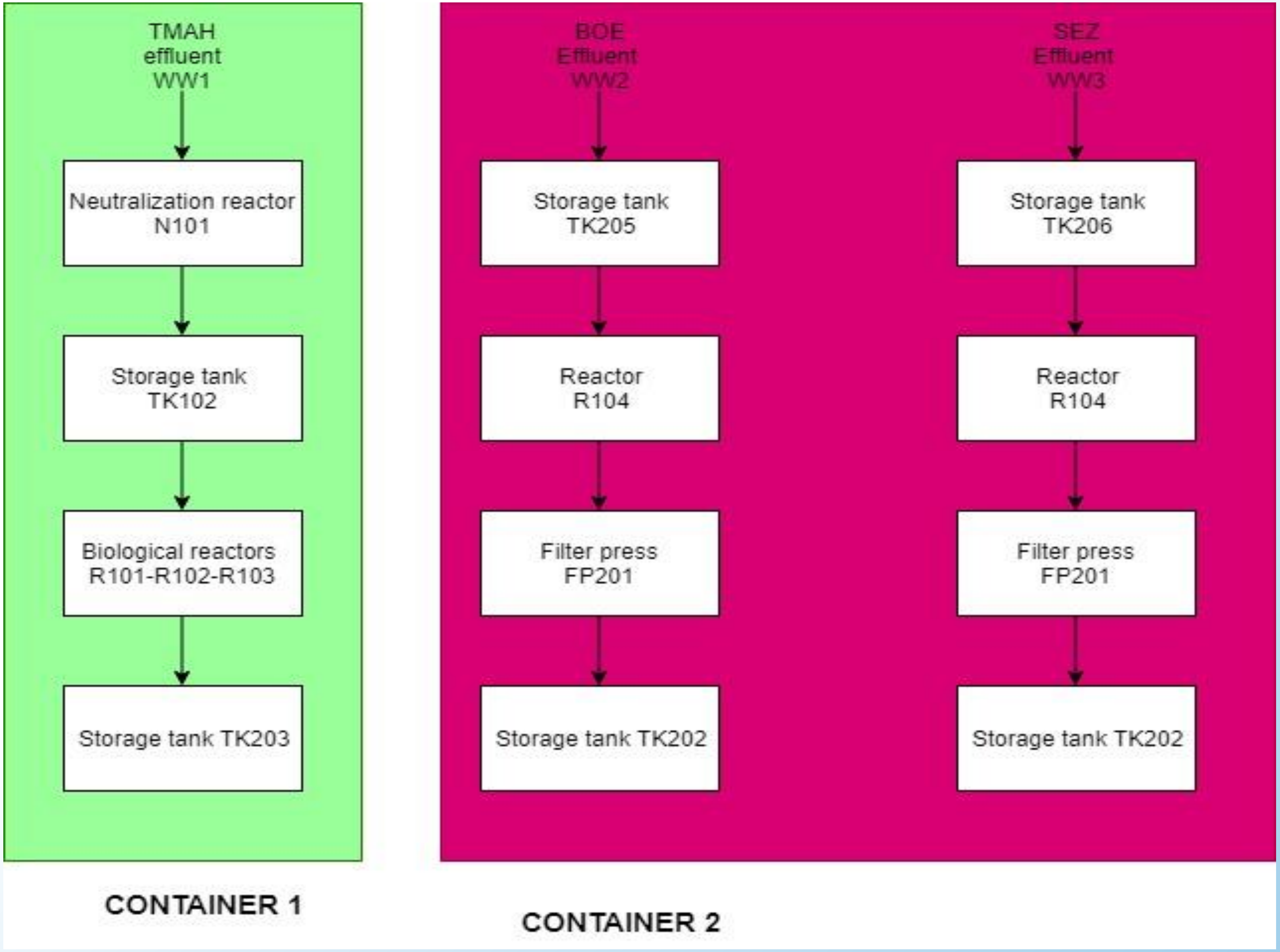
Optimal inlet pressure = 4 bar
Maximum degradation yields at pH 12 = 10%
Maximum degradation yields at pH 3 = 40%

Analysis of variance was applied to investigate, more in details, the effect of two factors on system response.

LIFE BITMAPS: process design



LIFE BITMAPS: organization of the 2 containers



LIFE BITMAPS: pilot plant – Container 1



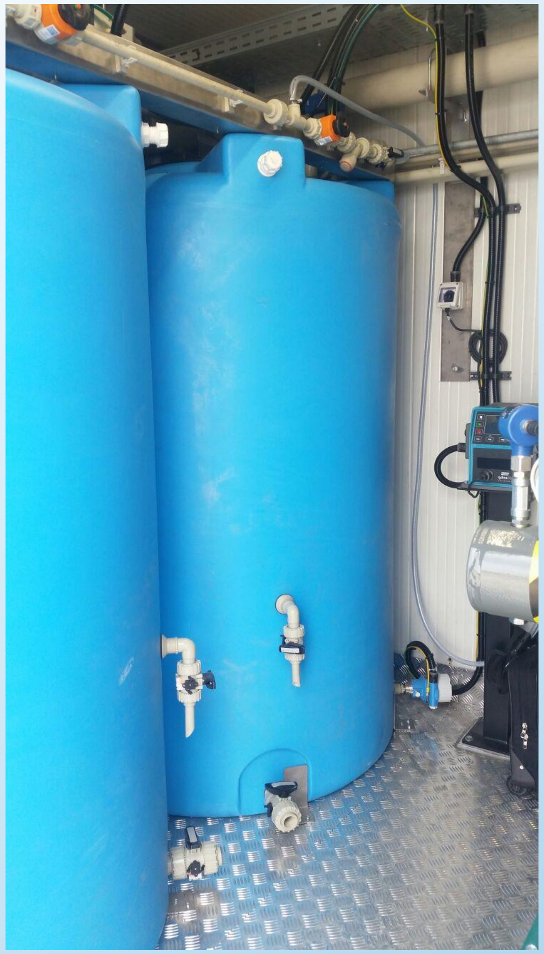
General overview of the mobile pilot plant



Neutralization of TMAH and N°3 bio-reactors in series

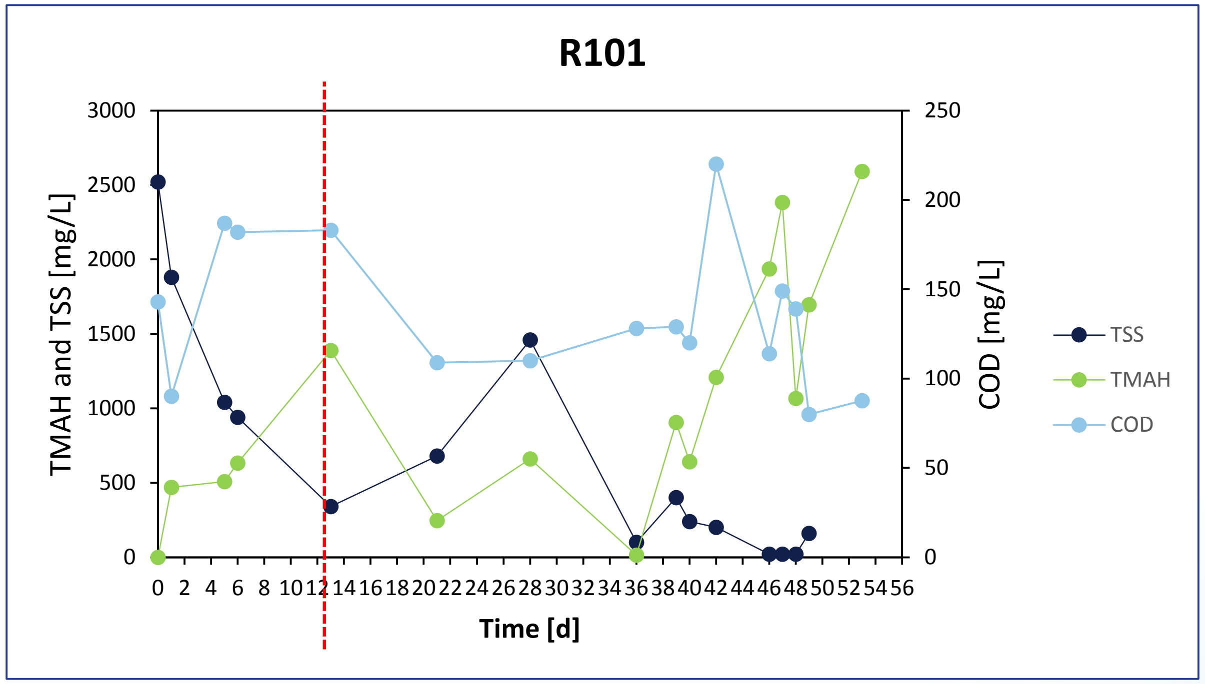
LIFE BITMAPS: pilot plant – Container 2

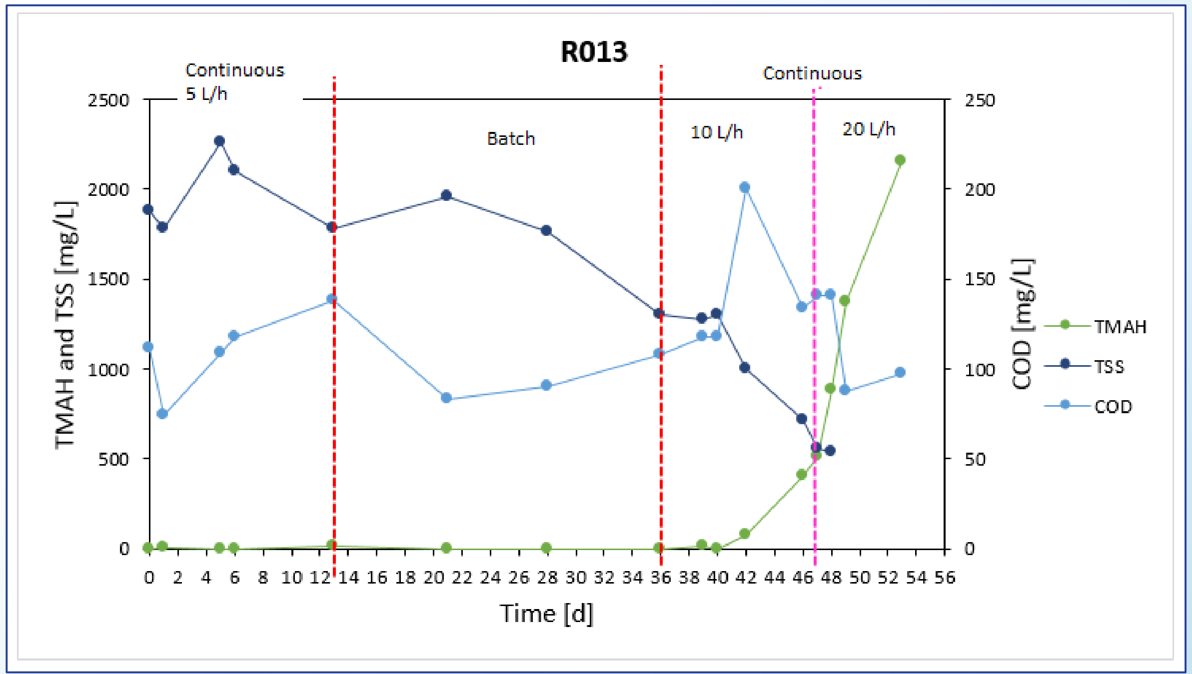


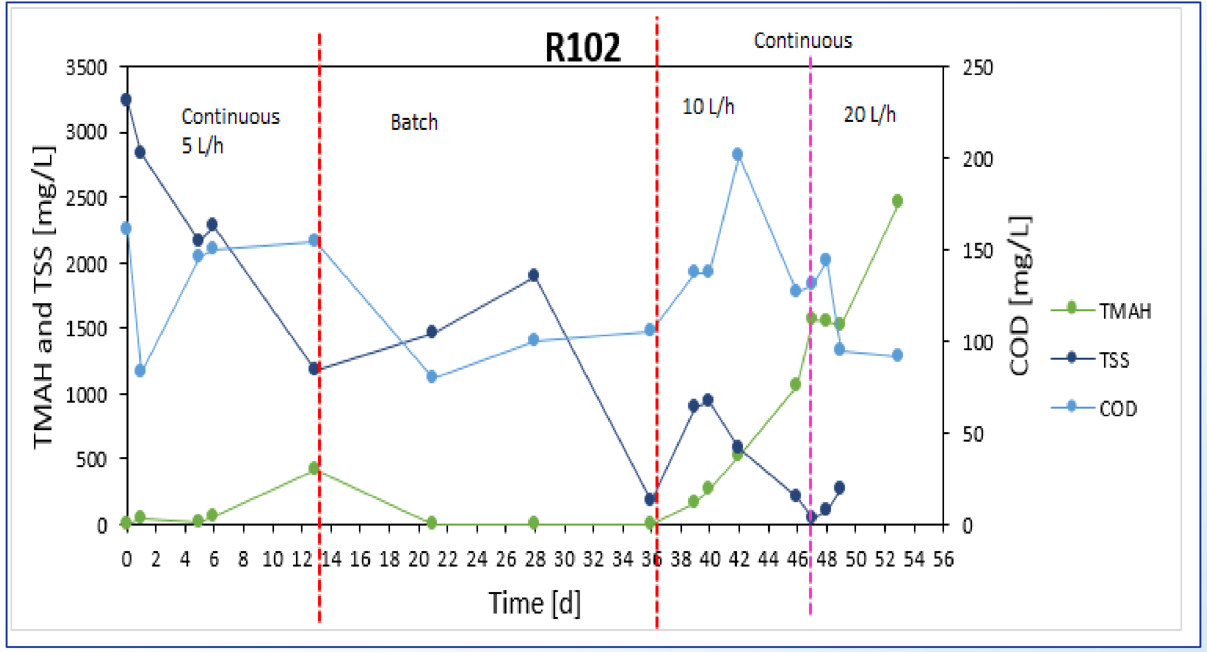



Container for the treatment of BoE and SEZ

LIFE BITMAPS: overview of pilot plant's tests





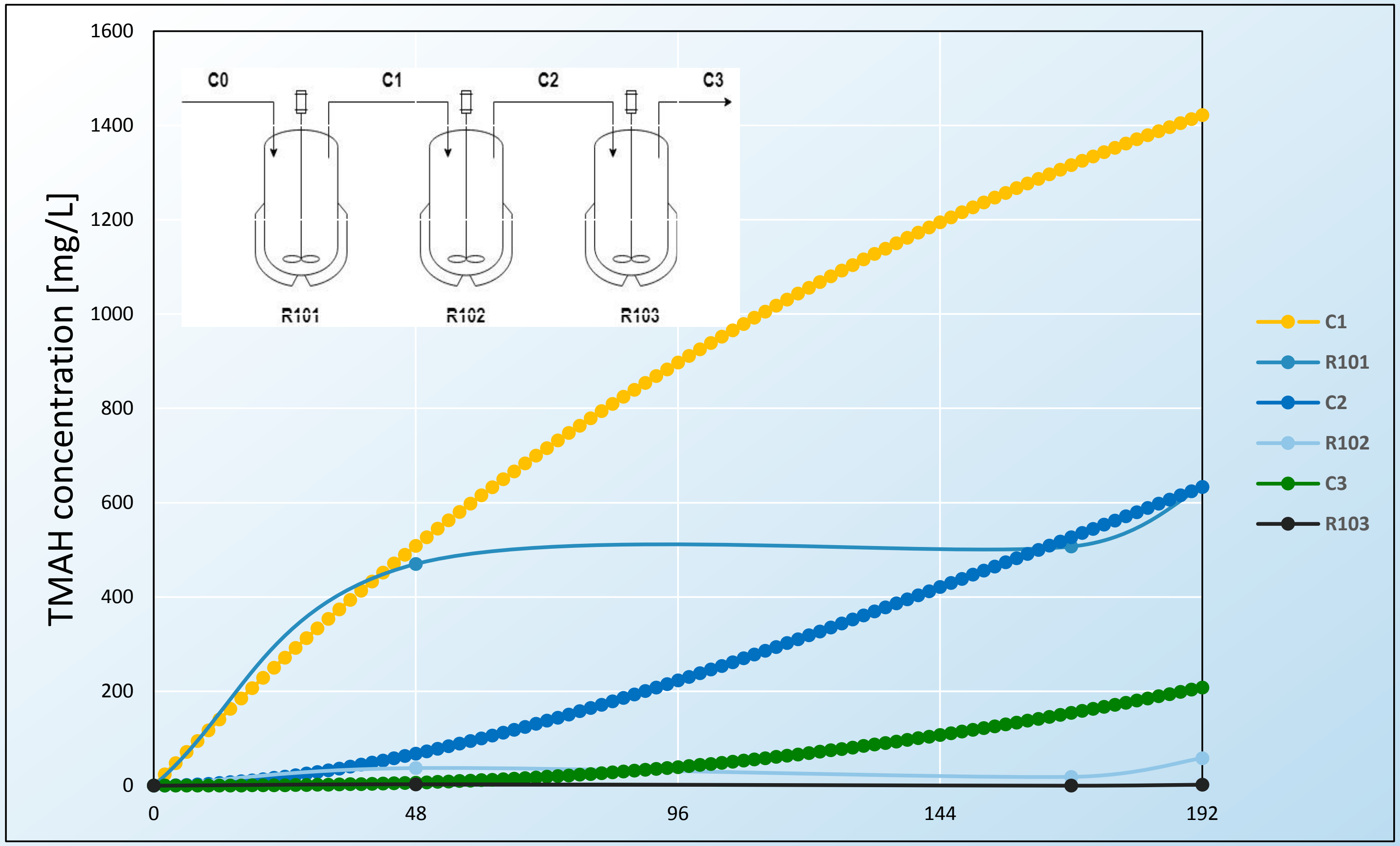


Overview of some experimental results in the 3 bioreactors R 101, R 102 and R 103 :

- **TMAH (mg/L)**
- **Total Suspended Solid – TSS (mg/L)**
- **COD (mg/L)**

Biological test of degradation of TMAH

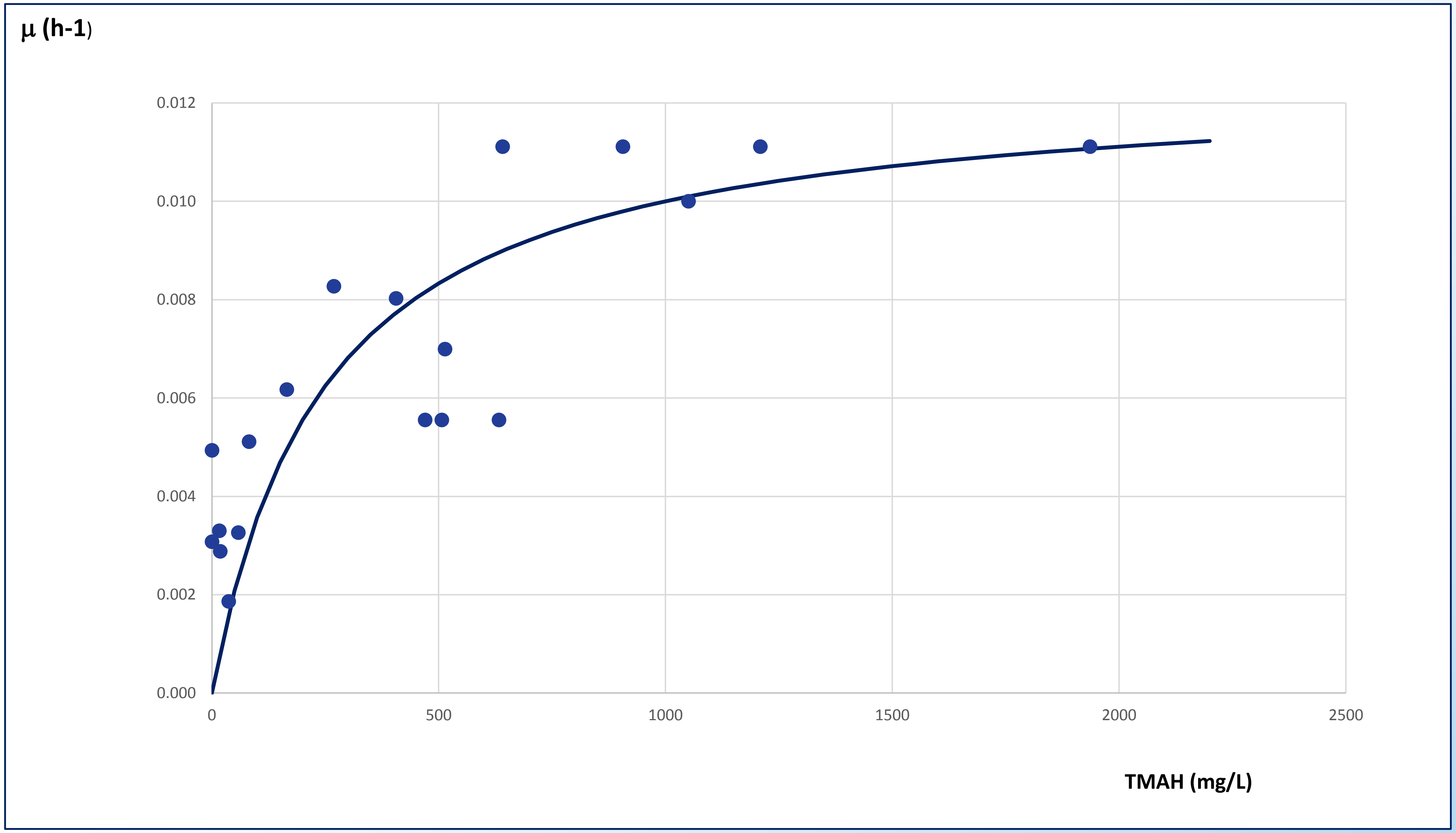
LIFE BITMAPS: pilot plant biological tests



Time [h]	R101	R102	R013
48	7.53%	45.10%	55.38%
168	61.46%	96.47%	99.97%
192	55.48%	90.82%	99.02%

TMAH biodegradation yield (5 L/h of neutralized feed as-is)

LIFE BITMAPS: data analysis of biological tests

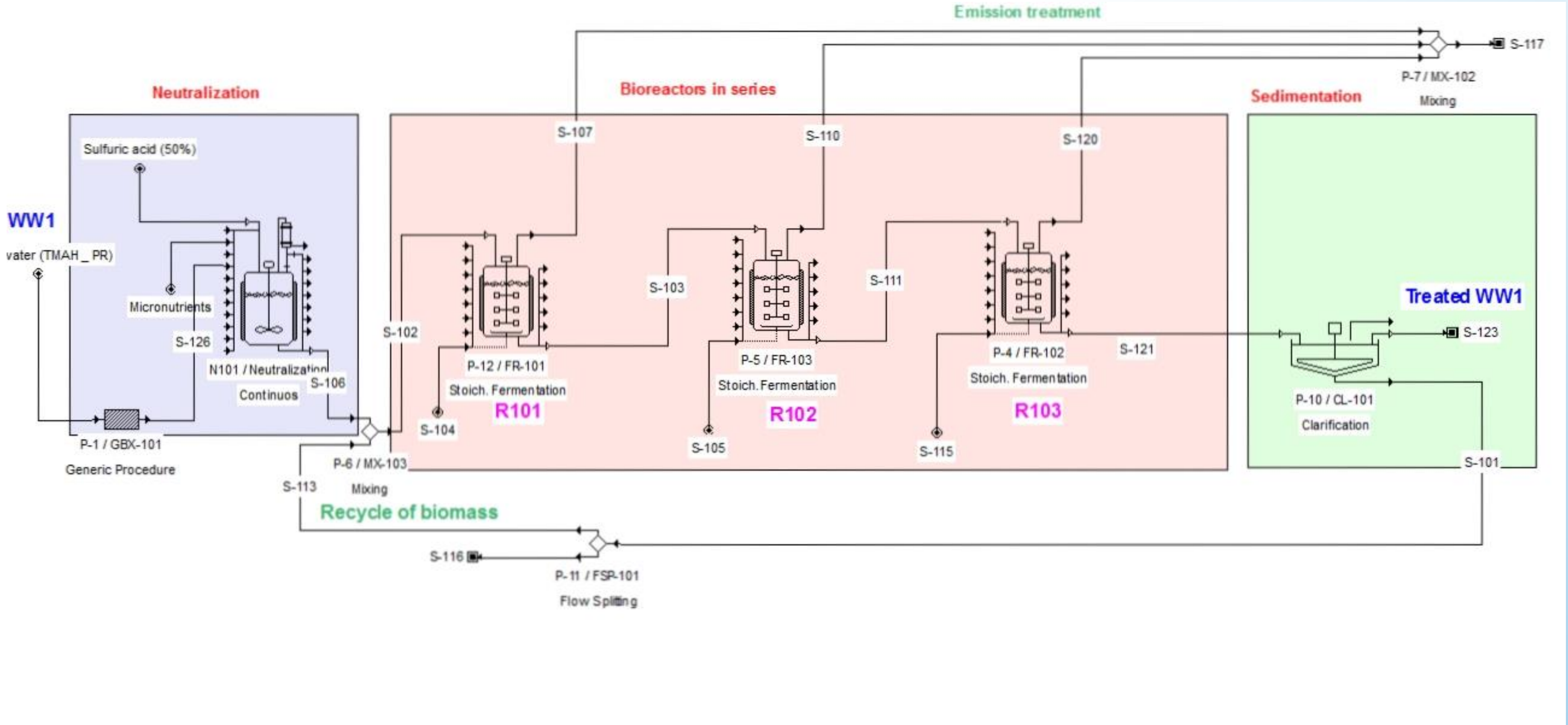


Parameters of Monod model:

- **μmax = 0,012 h-1**
- **Ks = 250 mg/L**

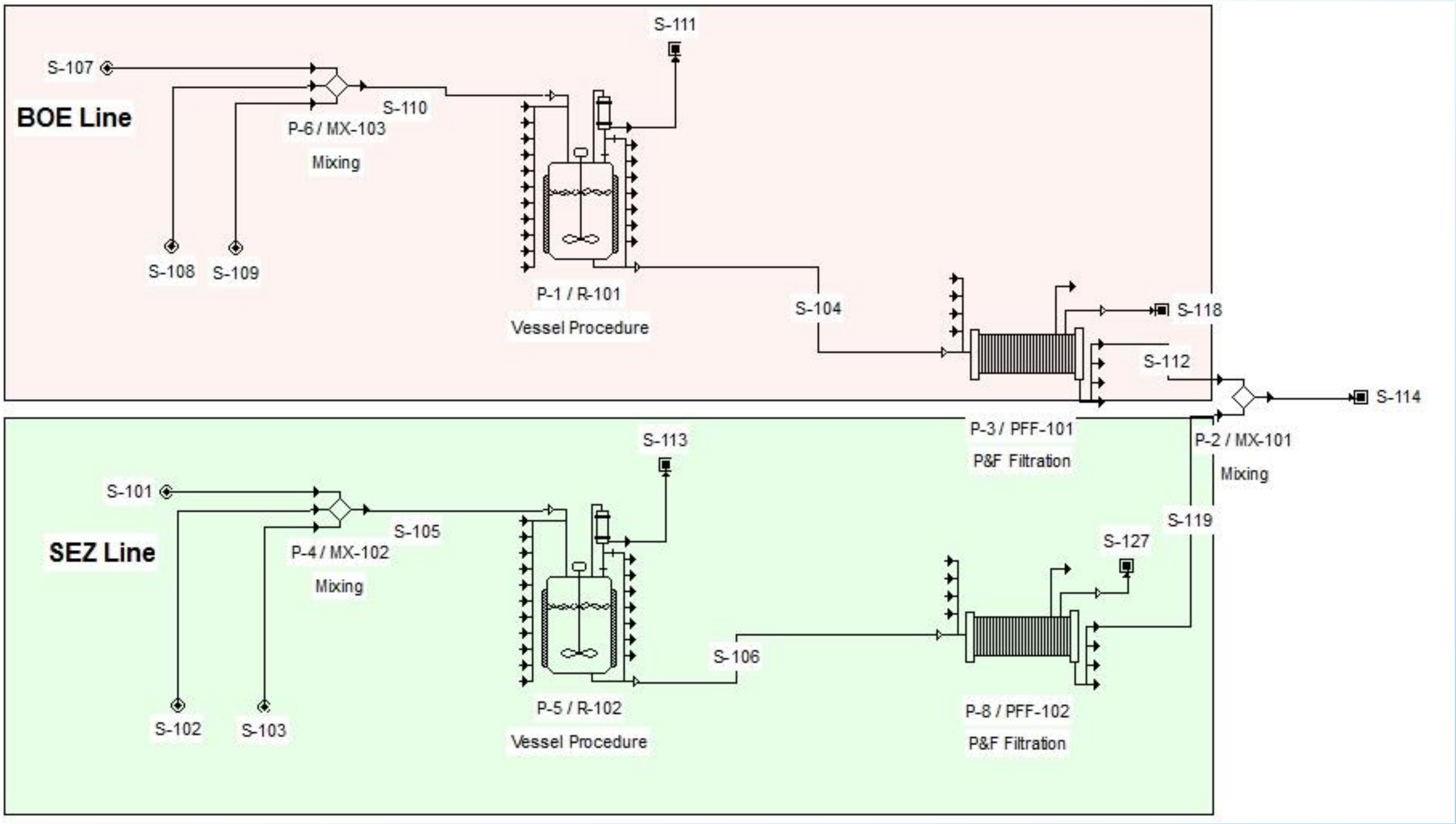
$$\mu = \frac{\mu max\ S}{Ks + S}$$

LIFE BITMAPS: Industrial Plant Design 1/2



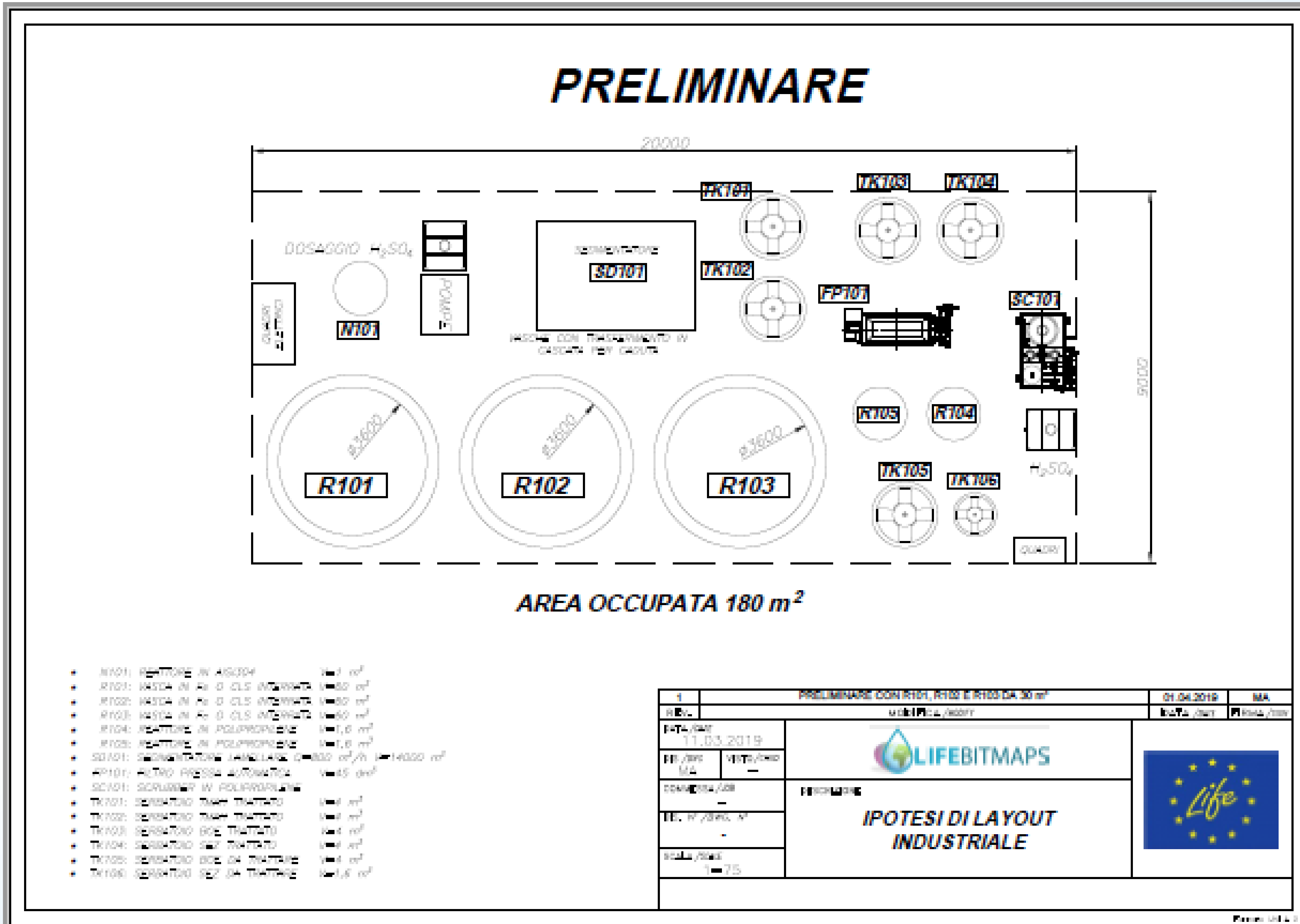
V R101 = V R102 = V R103 = 30 m3 (to treat 500-600 L/h of TMAH)

LIFE BITMAPS: Industrial Plant Design 1/2



Chemical precipitation of SEZ and BoE: V R101= V R102 = 2 m3

LIFE BITMAPS: lay-out



LIFE BITMAPS: Conclusions

Main conclusions (pilot scale):

1. Concentration of TMAH by UF+RO was demonstrated;
2. TMAH biodegradation with nitrification process was demonstrated;
3. Chemical treatment BoE and SEZ was demonstrated;
4. Pilot plant’s technical problems highlighted and resolved;
5. Integration of this process with WWT was demonstrated;
6. Preliminary design of treatment in industrial scale (done);
7. Economical evaluation (in progress);
8. Feasibility study (in progress): positive results;
9. Customized solutions;
10. LCA – in progress;

Thank You very much for your attention !

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