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

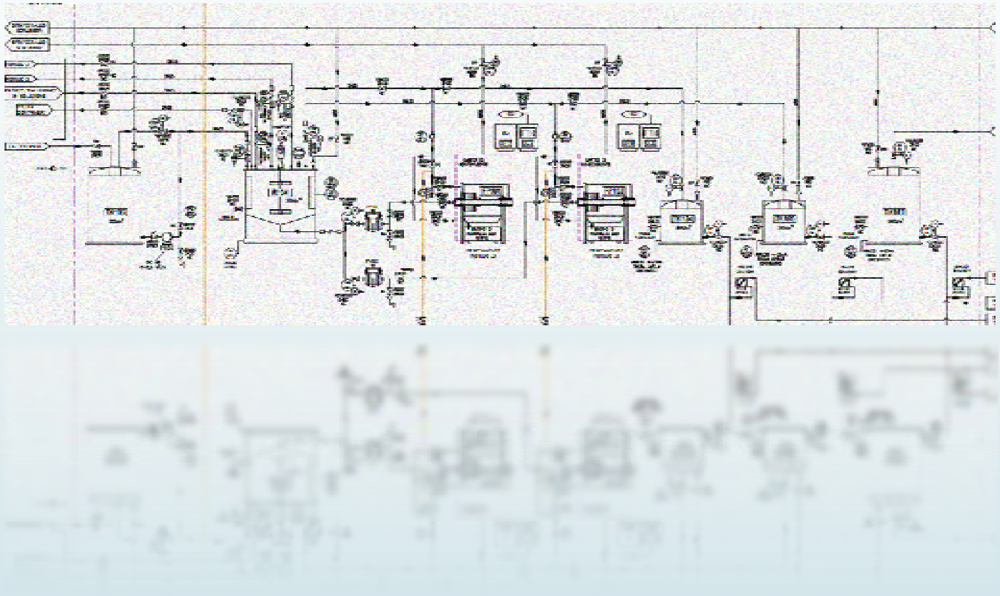
Prof. Eng.
Francesco Vegliò

L'Aquila 31 Maggio 2017
Aula Magna DSU
Università degli Studi dell'Aquila

This research was financially supported by the European Union within the "LIFE BITMAPS" Project LIFE15 ENV/IT/000332.

MAIN OBJECTIVES OF THE PROJECT

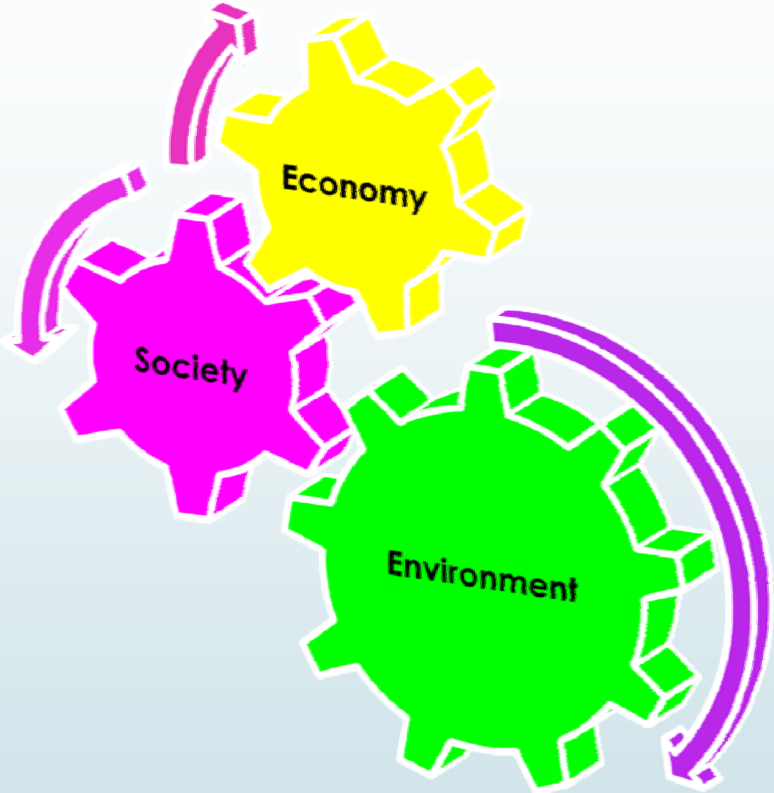
I. **Design, construction and validation of a semi-industrial pilot plant enabling the treatment of spent photoresist/tetramethylammonium hydroxide (PR/TMAH), and other mixed solutions generated by the E&S (Electronic & Semiconductor) manufacturing processes.**



II. Demonstrate, at industrial scale, the biodegradation of TMAH to non-toxic biomass plus NH3 by using some specific savage microorganisms selected during the previous R&D phase.

MAIN OBJECTIVES OF THE PROJECT

III. Prove the cost sustainability of the process



IV. Set up a more efficient water management approach proving that it is possible to reduce the net water consumption by saving water and evaluate the total reuse of treated wastewater in the company's industrial plant.

PARTNERS OF THE PROJECT

- ✓ **Lfoundry**
  Industrial partner -Responsible
  (Provided wastewater, support for all activities)

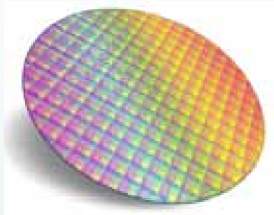
- ✓ **Univaq**
  Scientific partner
  (Laboratory tests of biodegradation, hydrocavitation and process analysis)

- ✓ **BME Biomaterials & Engineering S.R.L.**
  (Process analysis)

- ✓ **B.F.C. Sistemi Srl**
  (designs and constructs chemical plants and mechanical systems for industry)

PROJECT DESCRIPTION

A large amount of wastewater containing tetramethylammonium hydroxide (TMAH) is generated each year in Europe by electronics' and semiconductor manufacturers



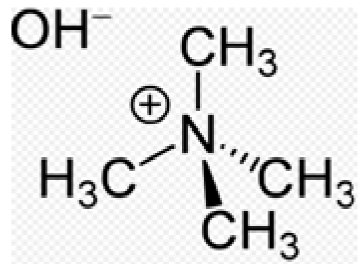
Because of the toxic properties of TMAH, for adequate protection of aquatic ecosystems, industrial streams containing TMAH require further treatment before they can be discharged into drainage systems

Current approaches to treatment of wastewater containing TMAH entail high costs for companies and negative environmental impacts.

Development of an innovative process for the degradation of TMAH by biological treatment and hydrocavitation

DANGEROUSNESS OF TMAH

During the process of realization of integrated circuits, tetramethylammonium hydroxide, also known as TMAH it is used.



This substance is a quaternary ammonium salt and it is a:

- compound odorless when pure
- corrosive and attack various plastics and rubbers
- turns out to be harmful to humans if ingested, inhaled or brought into contact with eyes or skin.

Environmental effects have not been studied at all: today is know that the TMAH is lethal to aquatic species (small fish, seaweed, shellfish)

Laboratory activities

LIFE BITMAPS - Pilot technology for aerobic Biodegradation of spent TMAH Photoresist solution in Semiconductor industries

LIFE15 ENV/IT/000332

DEVELOPMENT OF THE BIOLOGICAL PROCESS – LAB SCALE

Materials and methods:

Biological tests are carried out in a cylindrical bioreactor BIOSTAT® B with a double glass and a capacity of 6 L, under batch condition with a control unit for setting parameters : temperature, velocity and Oxygen

Table 1: Operation parameters for the fermentator tests

Parameters	Value
Velocity	70 rpm
Temperature	25 °C
Oxygen	2- 5/L/min

DEVELOPMENT OF THE BIOLOGICAL PROCESS – LAB SCALE

Materials and methods:

Analysis

- **COD (HACH-Lange kit: LCK 514)**
- **pH (HI254 pH-meter)**
- **TMAH (Ion Chromatograph Donex DX5000)**
- **ammonium ions (HACH-Lange kit: LCK 302) concentrations**

FEED OF THE BIOLOGICAL REACTOR

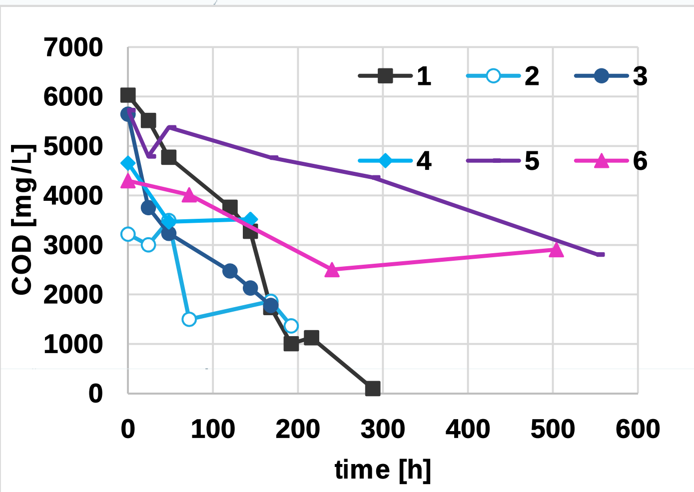
Wastewater

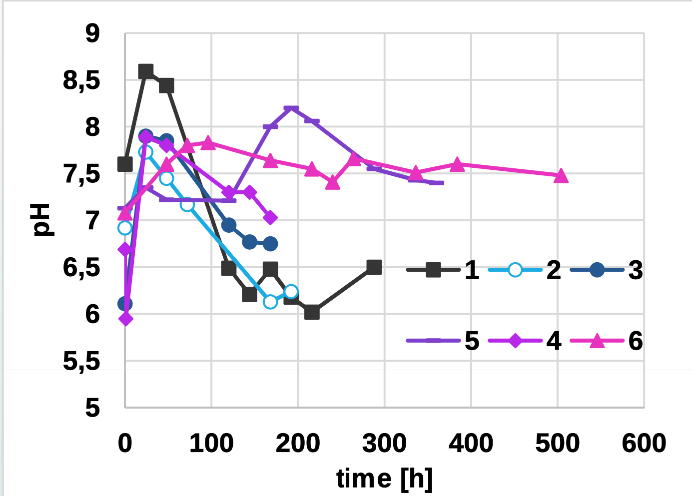
- TMAH
- PR (Photoresist) wich contains mainly 1-Methoxy-2-Propanol

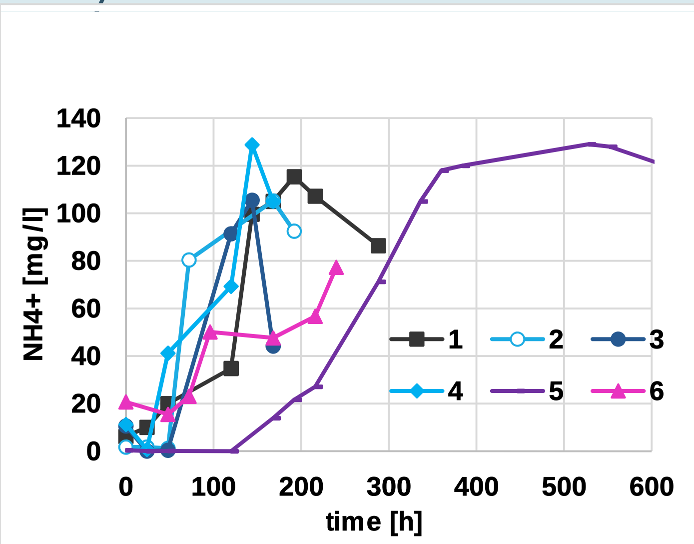
COMPOSITION OF THE CULTURE MEDIA	
Substance	Concentration [g/L]
$CuCl_2$	0.13
Na_2MoO_4	0.23
$NaHCO_3$	0.82
K_2HPO_4	0.21
$MgSO_4$	0.51
$FeCl_3$	0.1
Yeast extract	0.01

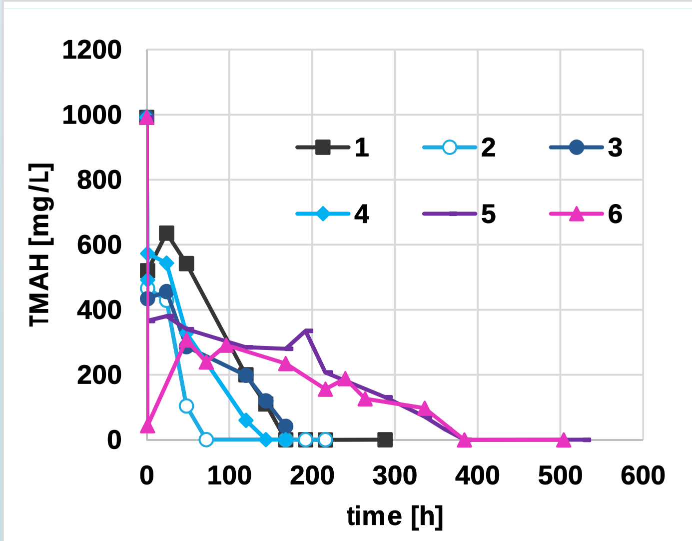
DEVELOPMENT OF THE BIOLOGICAL PROCESS – LAB SCALE

Results:

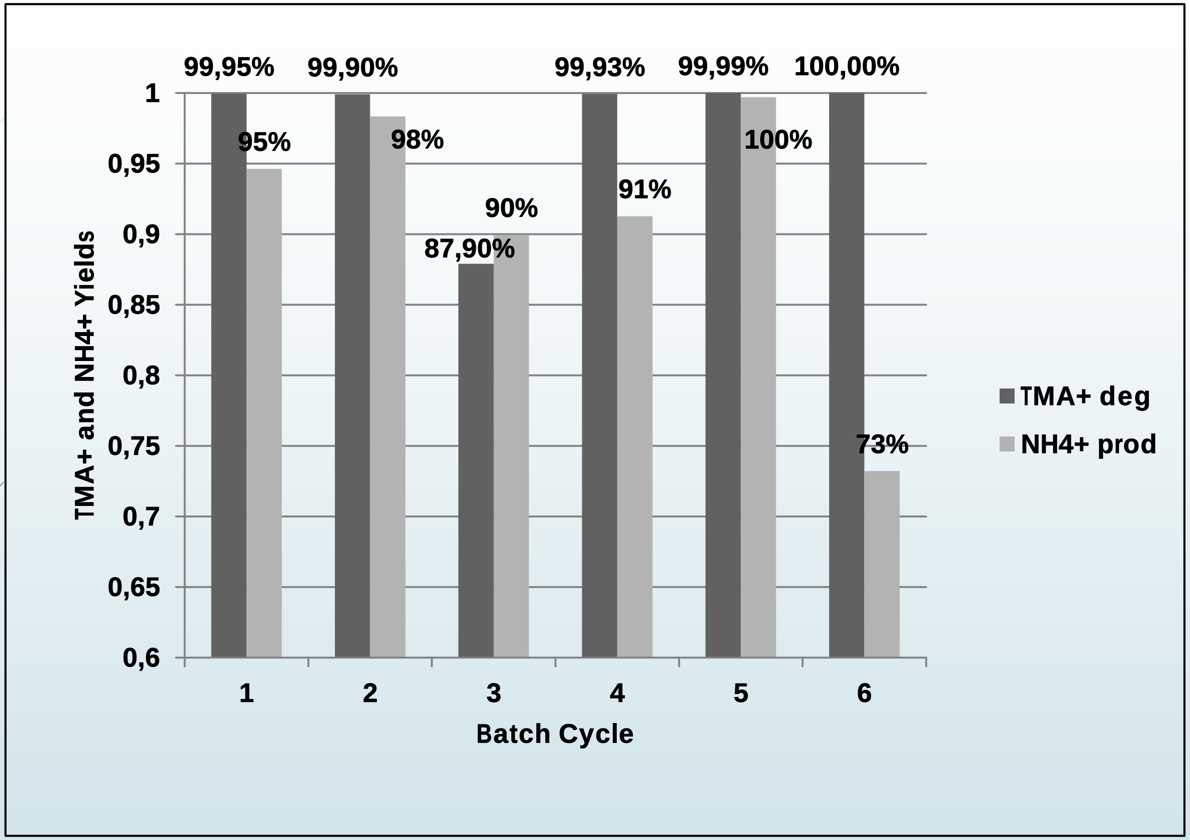








TMA+ degradation yield and NH4+ production yield



The experiments on wastewater have showed that biological treatment is able to remove TMAH with and efficiency greater than 99%, as TMAH removal yield, after about 6 days of process.

DEVELOPMENT OF THE BIOLOGICAL PROCESS – LAB SCALE

Stoichiometry biomass growth:

$$Substrate + O_2 \rightarrow Aerobic\ biomass + Products$$

$$C_4H_{12}N + a\ C_4H_{10}O_2 + b\ O_2 \rightarrow c\ CH_{1,7}O_{0,45}N_{0.20} + d\ CO_2 + e\ NH_3 + f\ H_2O$$

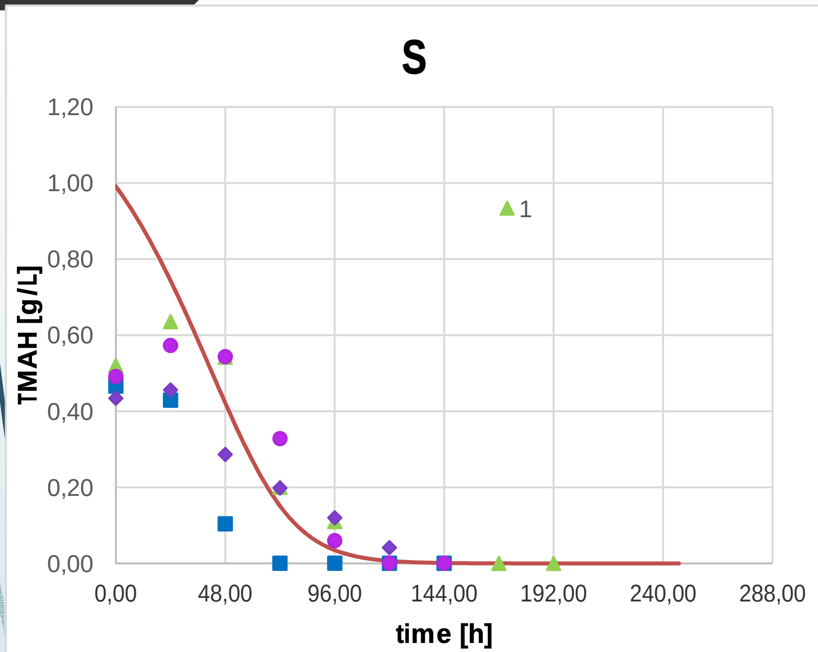
TMAH Photoresist

DEVELOPMENT OF THE BIOLOGICAL PROCESS – LAB SCALE

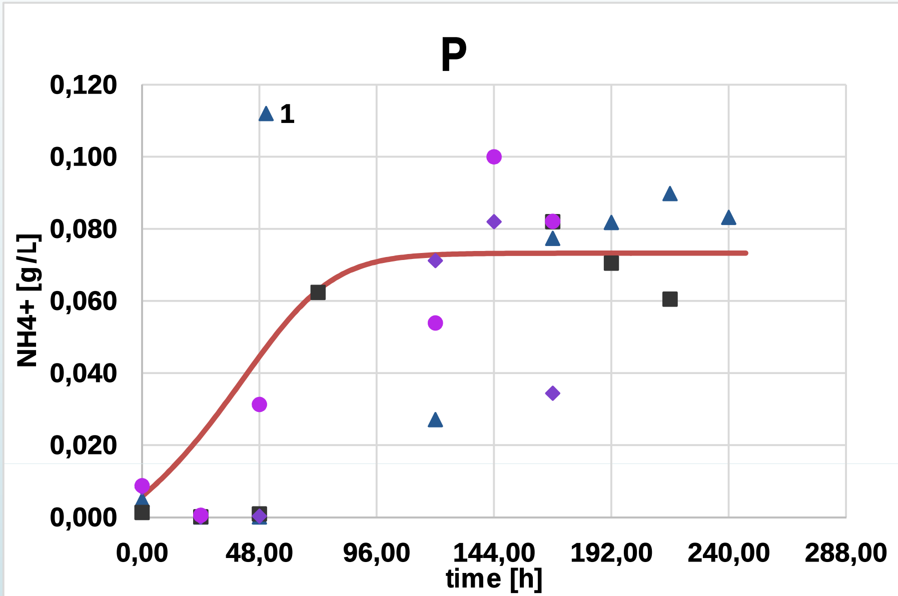
$$\begin{cases} \dfrac{dX}{dt} = \mu \cdot X \quad t = 0, \qquad X = X_0 \\ \dfrac{dS}{dt} = -\sigma \cdot X \; t = 0, \qquad S = S_0 \\ \dfrac{dP}{dt} = -\sigma \cdot X \; t = 0, \qquad P = P_0 \\ \mu = \mu_{MAX} \cdot \dfrac{S}{K_S + S} \\ \sigma = \dfrac{1}{Y^G_{X/S}} \cdot \mu + m \\ \pi = \alpha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

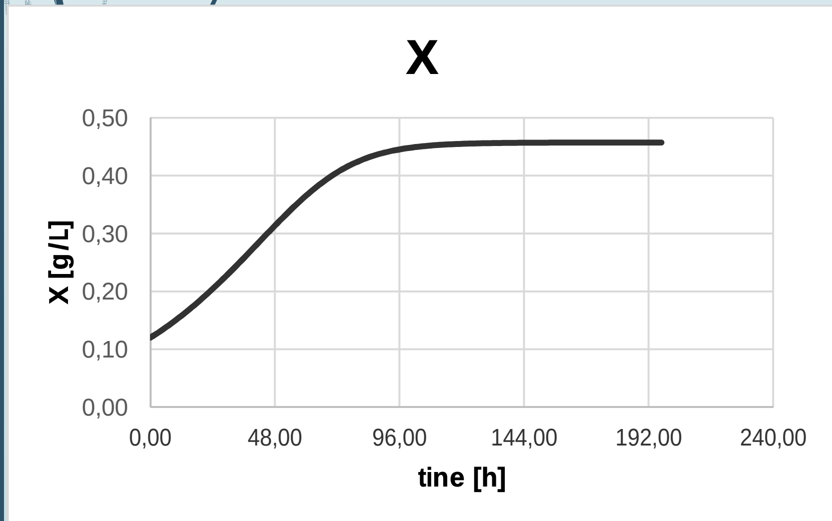
System resolution provides the following kinetic parameters: μ_{MAX} K_S $Y_{X/S}$

DEVELOPMENT OF THE BIOLOGICAL PROCESS – LAB SCALE



Solution of the system of equations for batch reactor





- S_0 = 0,992 g/L;
- X_0= 0,12 g/L;
- P_0 =0,006 g/L
- μ_{MAX}= 0,42 h^{-1};
- K_S = 0,8 g/L;
- $Y_{X/S}$ = 0,34

Process Analyis

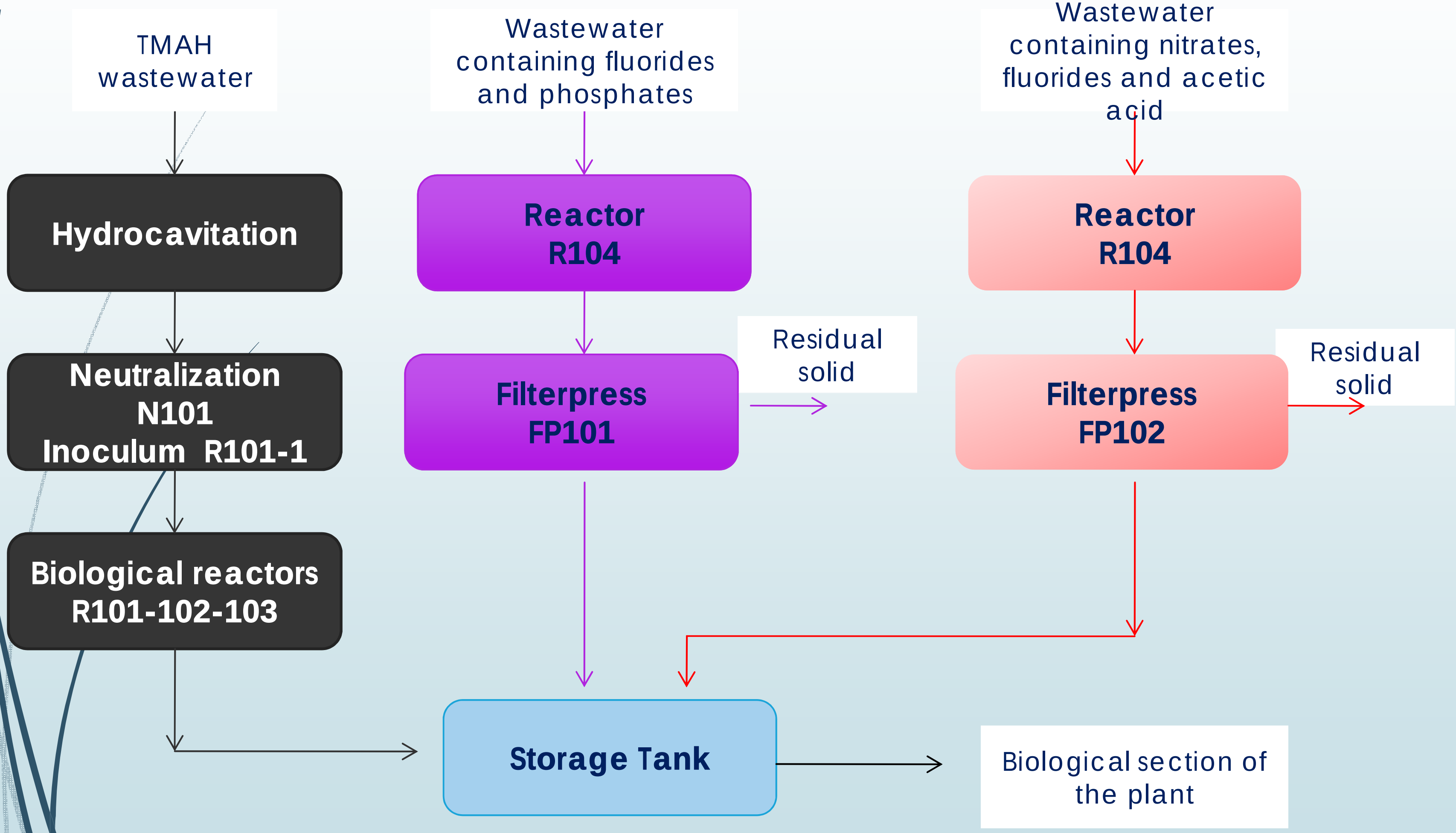
LIFE BITMAPS - Pilot technology for aerobic Blodegradation of spent TMAH Photoresist solution in Semiconductor industries

LIFE15 ENV/IT/000332

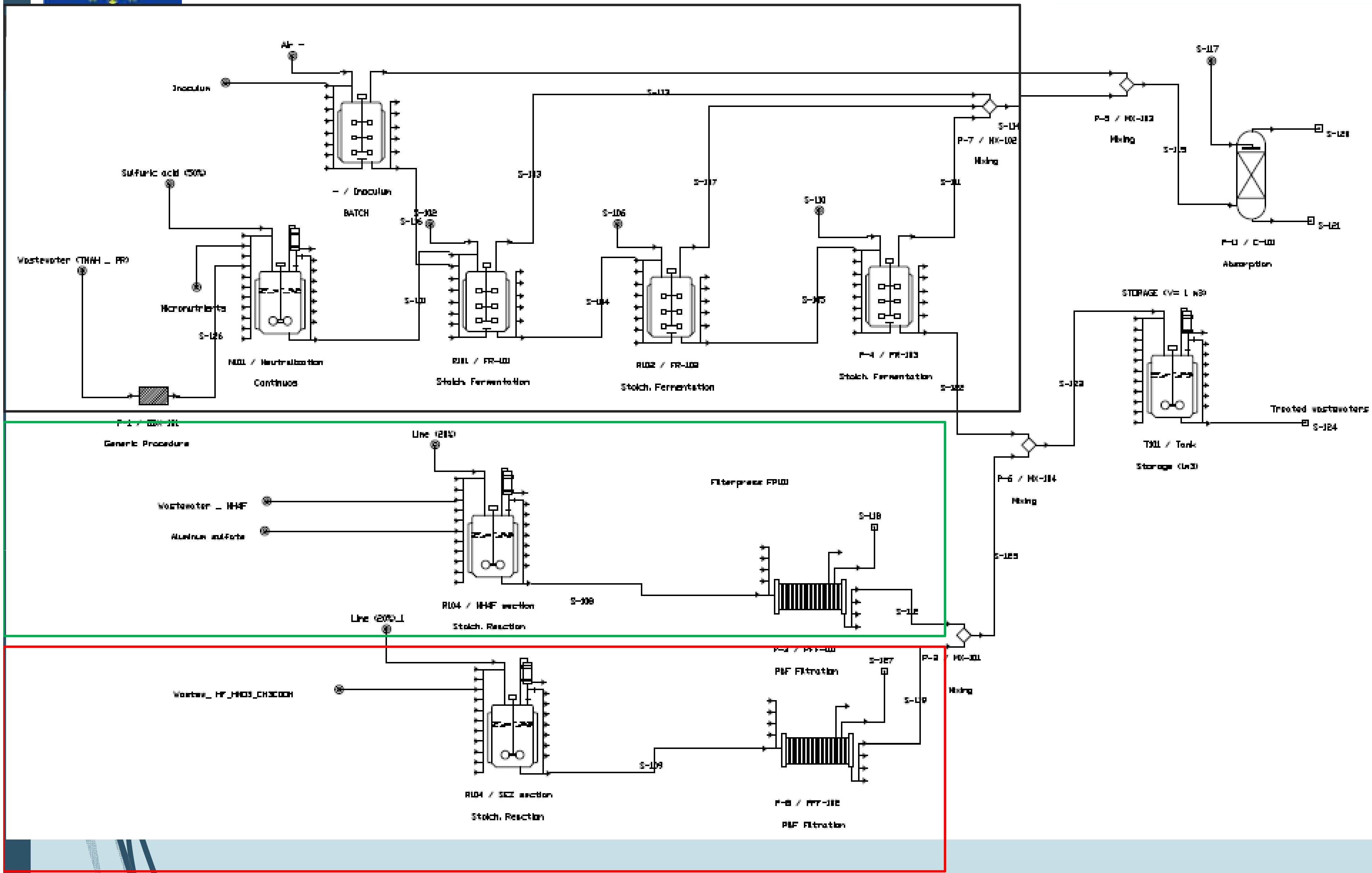
The same pilot plant treats other two types of wastewater that contain mainly fluorides, nitrates, acetic acid, ...

These wastewaters are treated using chemical-physical operations already validated in laboratory scale

Block scheme of the plant



Simulation of the process



Simulation of the process

Input - Wastewater	Unit
WastewaterTMAH Line 1	**25 kg/h**
Wastewater Line 2	**60 kg/d**
Wastewater Line 3	**16 kg/d**

Input – Reagents – Line 1	kg/h
Sulfuric acid for neutralization	0.1

Input – Reagents - Line 2	kg/d
Lime solution	21.84
Aluminum sulfate	2.4

Input – Reagents - Line 3	kg/d
Lime solution	9.29

Simulation of the process

Output –Line 1	kg/h
Treated wastewater	27

Output– Line 2	kg/d
Treated wastewater	75
Residual solid	9

Output – Line 3	kg/d
Treated wastewater	24.6
Residual solid	1.28

Simulation of the process

Line 1

Removal yield of TMAH

1. 52% R101
2. 75% R02
3. 83% R103

Total yield: 98%

Line 2

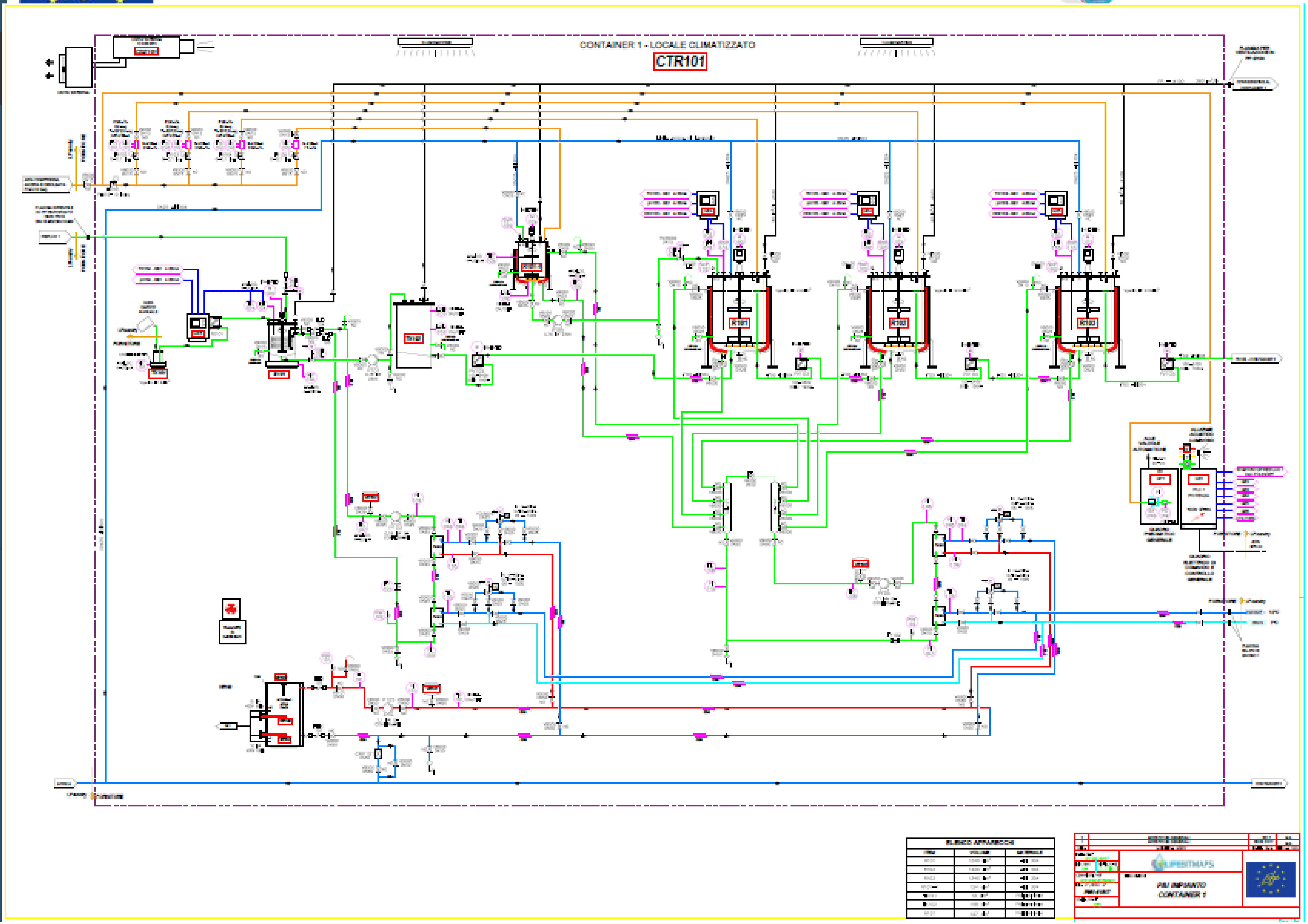
Reaction yields for the removal of the impurities ~100%

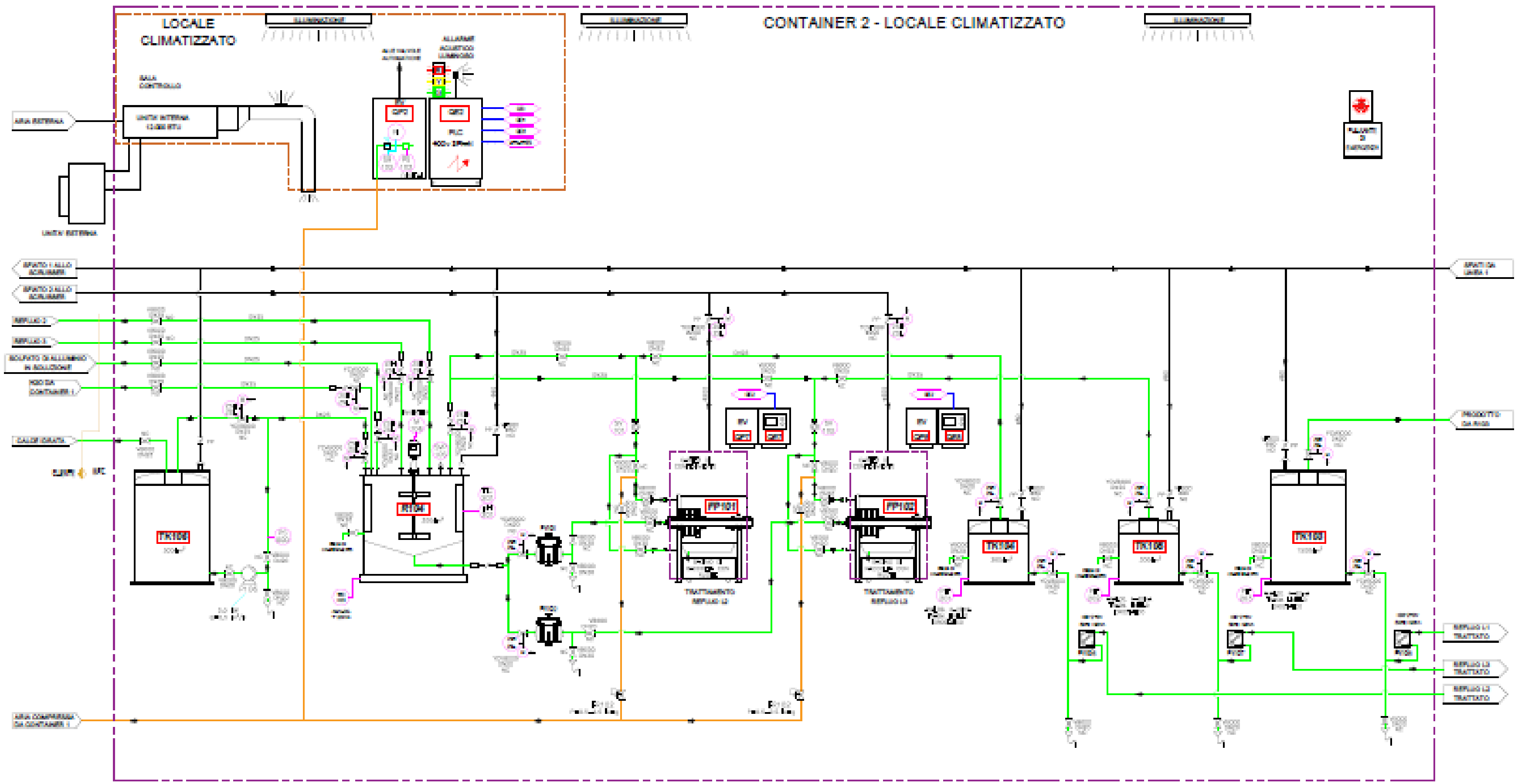
Line 3

Reaction yields for the removal of the impurities ~100%

EQUIPMENT SUMMARY (2017 prices)

Name	Type	Units	Standby/ Staggered	Size (Capacity)		Material of Construction	Purchase Cost (€/Unit)
R101	Reactor	1	0/0	1,300.00	L	Plastic	5,000
R102	Reactor	1	0/0	1,300.00	L	Plastic	5,000
R103	Reactor	1	0/0	1,300.00	L	Plastic	5,000
N101	Reactor	1	0/0	33.80	L	Plastic	2,000
R101-1	Reactor	1	0/0	133.33	L	Plastic	2,000
R104	Reactor	1	0/0	130.00	L	Plastic	3,000
C-101	Absorber	1	0/0	1,178.10	L	Plastic	20,000
Tank	Reactor	1	0/0	1,000.00	L	Plastic	5,000
Cabvitation	Generic Box	1	0/0	25.11	kg/h	CS	20,000
PFF-101-2	Plate & Frame Filter	1	0/0	0.51	m2	SS316	50,000


CONTAINER 1 - LOCALE CLIMATIZZATO
CTR101
ELENCO APPARECCHI
P&I IMPIANTO
CONTAINER 1



ELENCO APPARECCHI		
ITEM	VOLUME	MATERIALE
[illegible]	[illegible] dm³	[illegible]
FP101	— dm³	[illegible]
FP102	— dm³	[illegible]
[illegible]	[illegible] dm³	[illegible]
TK104	500 dm³	[illegible]
TK105	500 dm³	[illegible]
TK106	500 dm³	[illegible]

P&I IMPIANTO
CONTAINER 2

Thank You

Prof. Eng. Francesco Vegliò
Department of Industrial Engineering, Information and Economy
University of L'Aquila
Monteluco di Roio

Contact:
francesco.veglio@univaq.it
Office tel: +39 0862 434223