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advanced environmental technologies

From bench to full scale AOP's application

SUMMER SCOOL

10-14 July 2017, Porto, Portugal

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13.07.2017

CORE BUSINESS

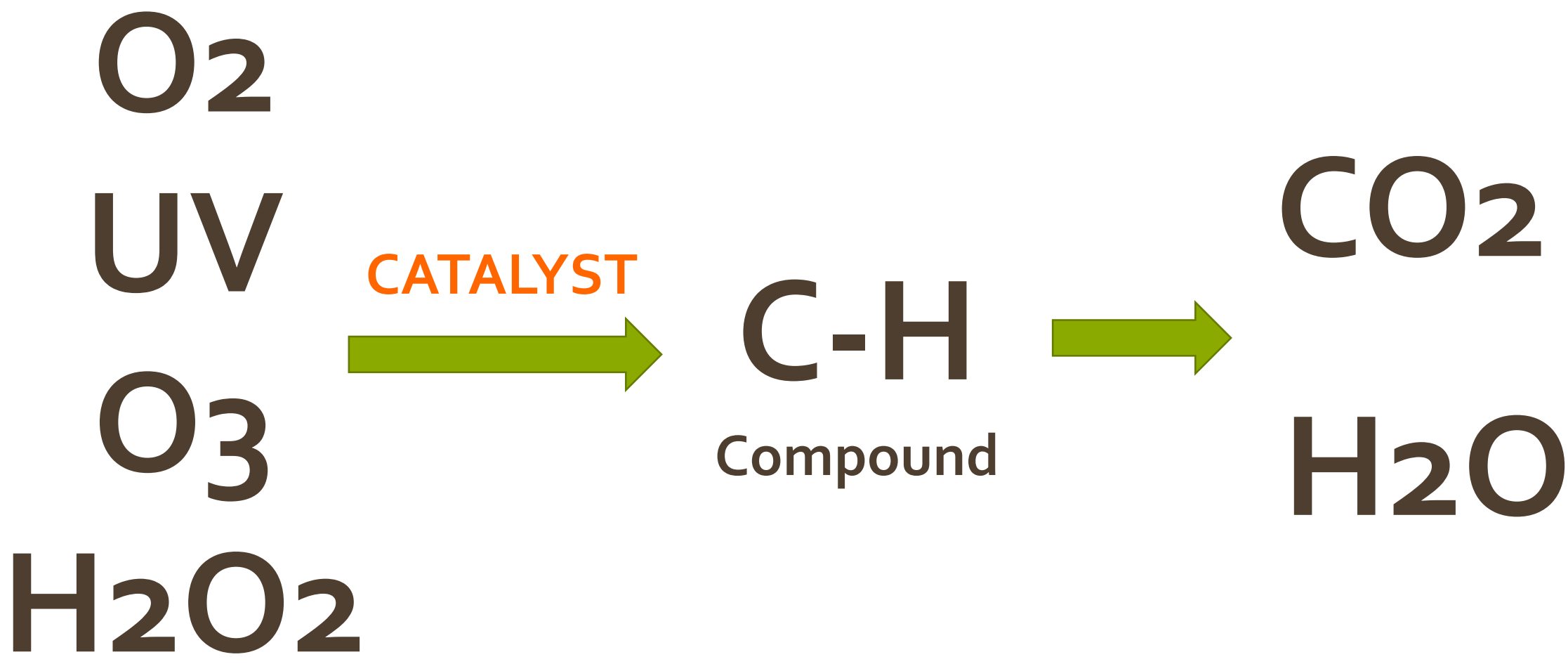
- Treatment of Industrial Effluents (water and waste gases)

- Use of AOP processes alone or coupled with conventional technologies

BENCH TO FULL SCALE

A O P

ADVANCED OXIDATION PROCESSES


O2
UV
O3
H2O2
CATALYST
C-H
Compound
CO2
H2O

WHY AOP ?

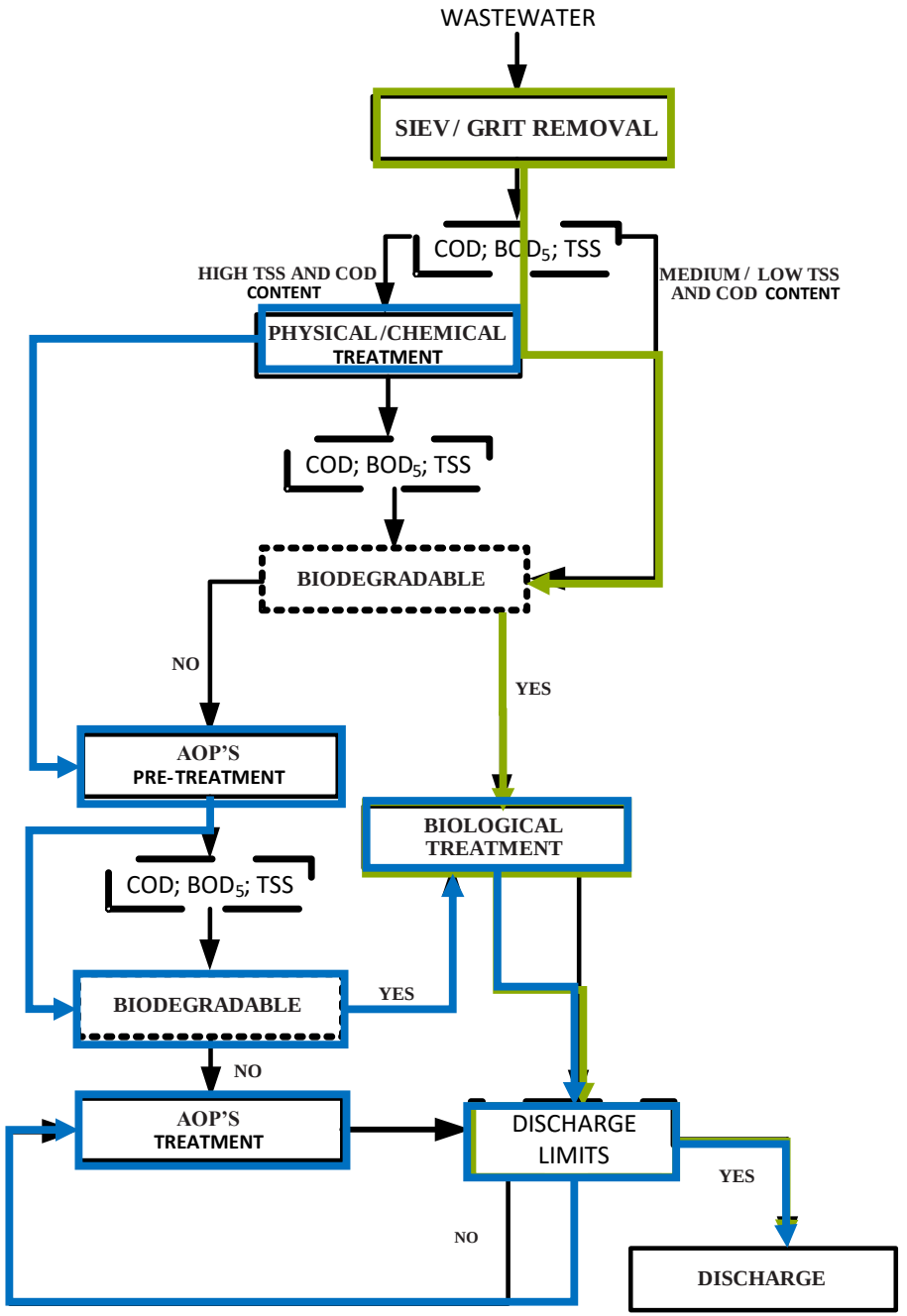
SOME ORGANIC COMPOUNDS ARE

NON-BIODEGRADABLE

TOXIC

FOR BIOLOGICAL PROCESSES

Processes Integration



Ideal

CASE 1 : FENTON (H_2O_2+$FeSO_4.6H_2O$)

Detergent

- 40 m3/day
- Discharge on Municipal Sewer
- Co (COD) = 20.000 – 30.000 mg O2/L
- C_{limit} (COD) = 1.250 mg O2/L
- Reactor Size = 20 m3
- Type: Batch / Semi-Batch

CASE 2 : COAGULATION + FENTON

OMW

- 30 m3/day
- Discharge on Municipal Sewer
- Co (COD) = 10.000 – 15.000 mg O2/L
- C_{limit} (COD) = 1.250 mg O2/L
- Reactor size: 2 + 60 m3
- Type: CSTR (2 different mix)

CASE 3 : O3

Rubber Pipe Extrusion

- 5 m3/day
- Discharge on Watercourse
- Co (COD) = 6.000 – 10.000 mg O2/L
- C_{limit} (COD) = 150 mg O2/L
- Reactor Size = 10 m3
- Type: Column, Continuous

CASE 4 : BIO + FENTON

Elderberry Processing

- 5 m3/day
- Discharge on Municipal Sewer
- Co (COD) = 8.000 – 12.000 mg O2/L
- C_{limit} (COD) = 450 mg O2/L
- Reactor Size: 10 m3
- Type: Batch / Semi-Batch

CASE 5 : O_3 + UV

Disinfection / Re-use
Process Water ; Bio Fungicide

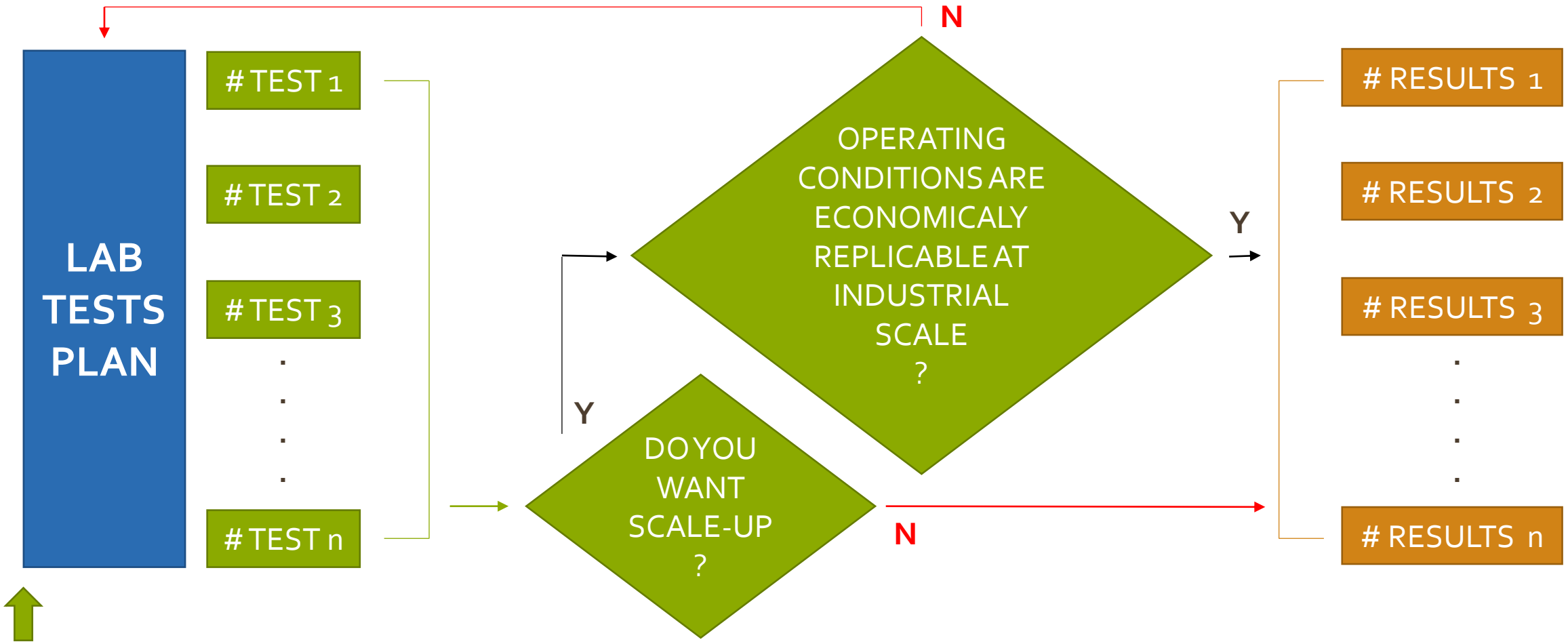
- 360 m3/day
- Process Water
- Re-use on Hydroponics
- TBC at 37°C = 1 x 10^5 cfu/mL
- Coliform = 5 x 10^2 N/100 mL
- E.Coli > 100 N/100mL

CASE 6 : BIO

Chips

- 600 m3/day
- Discharge Watercourse
- Co (COD) = 15.000 – 20.000 mg O2/L
- C_{limit} (COD) = 150 mg O2/L
- Reactor Size = 2.500 m3
- Type: Conventional AS

METHODOLOGY OF SCALE-UP



Scale-up starts here !

1ST APPROACH FOR REPLICABLE OPERATING CONDITIONS

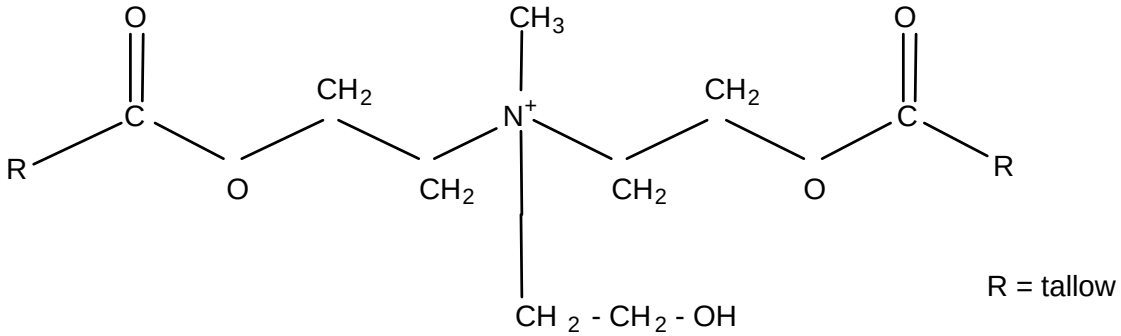
Parameter / Capacity Range (COD)		< 0,3 ton/d	0,3 – 3 ton/d	3 – 10 ton/d	> 10 ton/d
Type of Wastewater		INDUSTRIAL			MUNICIPAL
Typical Flowrate		< 20 m3/d	20 -200 m3/d	200 – 600 m3/d	> 20.000 m3/d
REACTOR DESIGN	Pressure (bar)	1 - 40	1 - 20	NTP	
	Temperature (ºC)	20 – 250	20 – 150		
	Hydraulic Retention Time (HTR)	40 – 0,5 h	40 – 2 h	40 – 10 d	5 – 10 d
	H2O2 (50%, 200 vol)	< 10 L/m3		< 5 L/m3	< 0,5 L/m3
	O3	< 200 g/m3			< 10 g/m3
	UV (LP lamps – 250 nm)	600 – 2400 J/m2 ; < 60 W/m3			< 600 J/m2 < 10 W/m3

FENTON SCALE-UP (Cases 1) – Detergent Industry

Great variability of Raw Wastewater

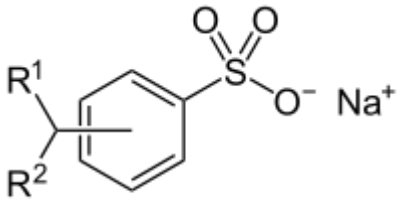
10.000 mg/L < **COD** < 100.000 mg/L

Main Chemical Compounds (Surfactants)



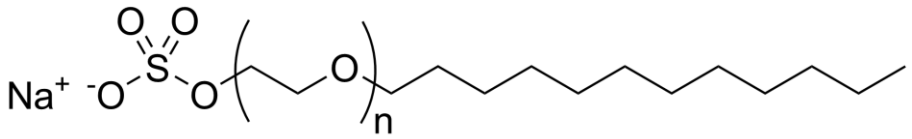
R = tallow

Stepantex VS 90 (esterquat)
(fabric softener)



$R^1 + R^2 = C_{11}H_{24}$

Dodecyl Benzene Sulfonic Acid
(Anionic Surfactant)



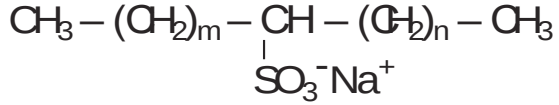
Sodium laureth sulfate
(Anionic Surfactant)

$RO(CH_2CH_2O)_XH$

$R = C_{10}H_{21}$

$x = 4, 5, 6, 7, 8, 9, 10, 14$

Lutensol® XL
(nonionic surfactant)

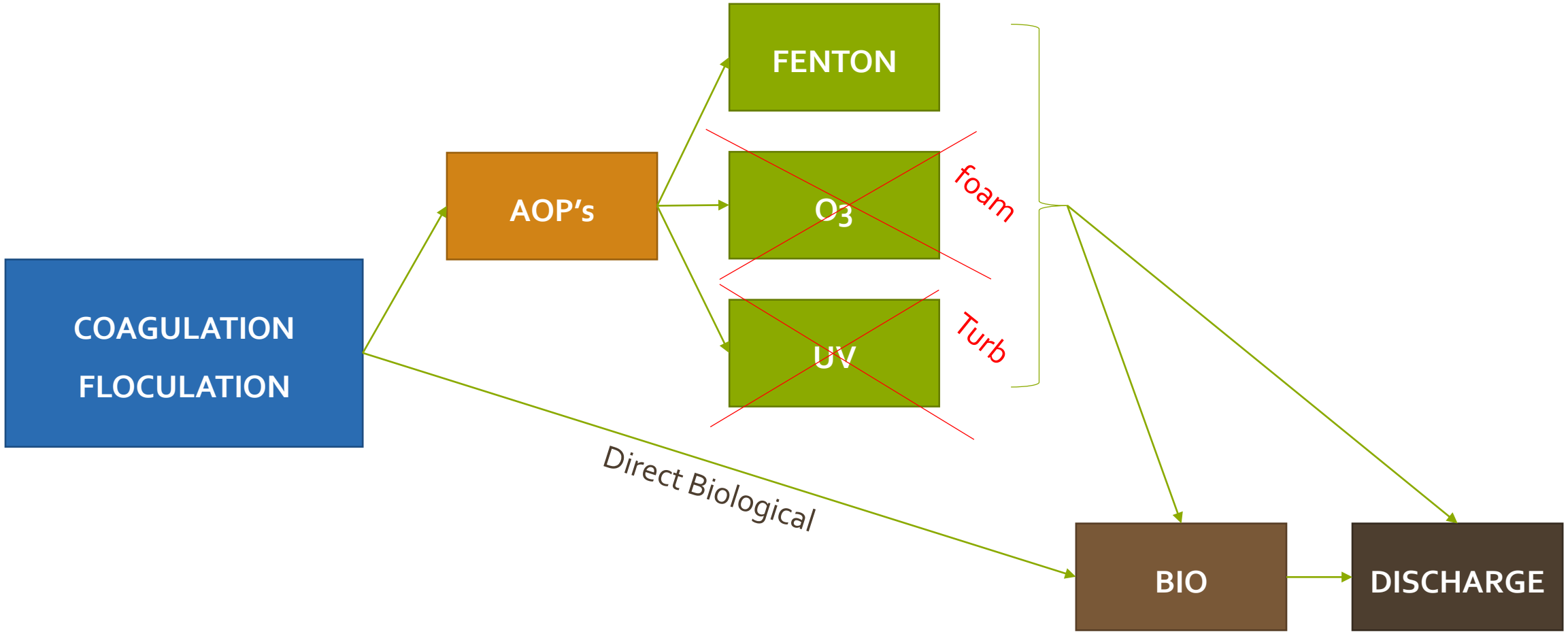


Sodium C14-17 sec-Alkyl Sulphonate
(Anionic Surfactant)

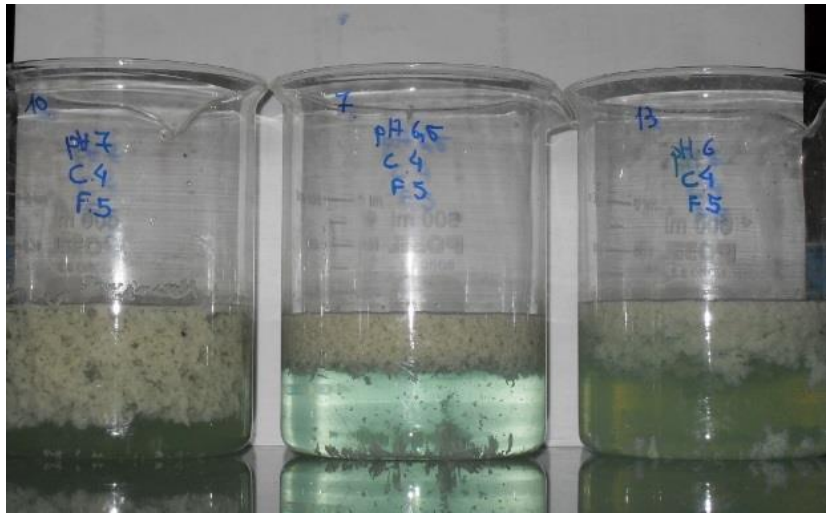
Main Requirements of the Client

- Discharge under Regulation Limits;
- Reuse old Plant as much as possible;
- Reuse old fibre glass reactor available on site (old process reactors);
- 40 m3/day

Lab Test Planning (CASE 1)



Coagulation / Flotation



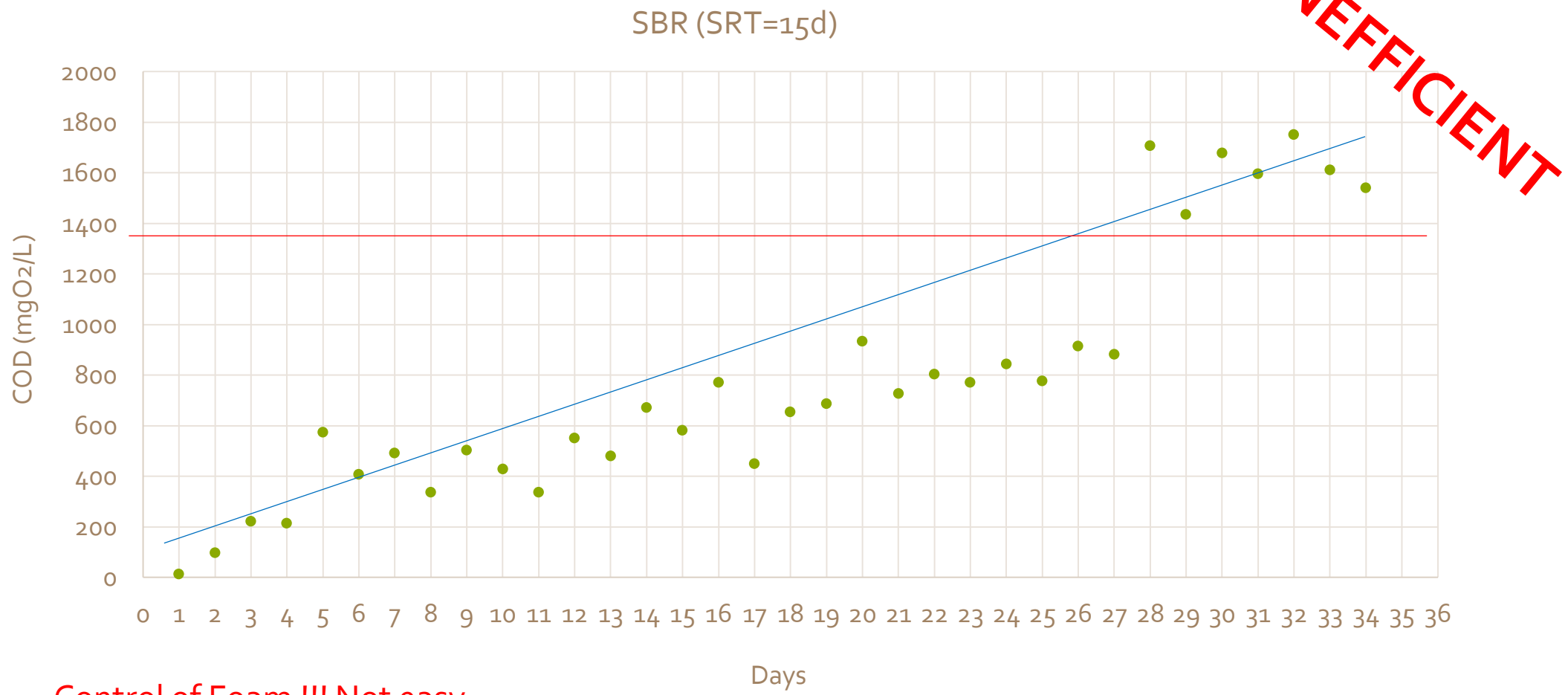
EFFICIENCY

30 – 60 %

Variability of the Raw Wastewater → Instability of the Coagulation/Flocculation Process

Direct Biological Process (After Coagulation / Flocculation)

UNEFFICIENT



Control of Foam !!! Not easy.

SCALE-UP CONSIDERATIONS

BEFORE SELECTING THE AOP'S TECHNOLOGIES, TAKE INTO CONSIDERATION THE LIMITATIONS OF EACH AOP

UV

- Turbidity / Suspended Solids (< 50 NTU)

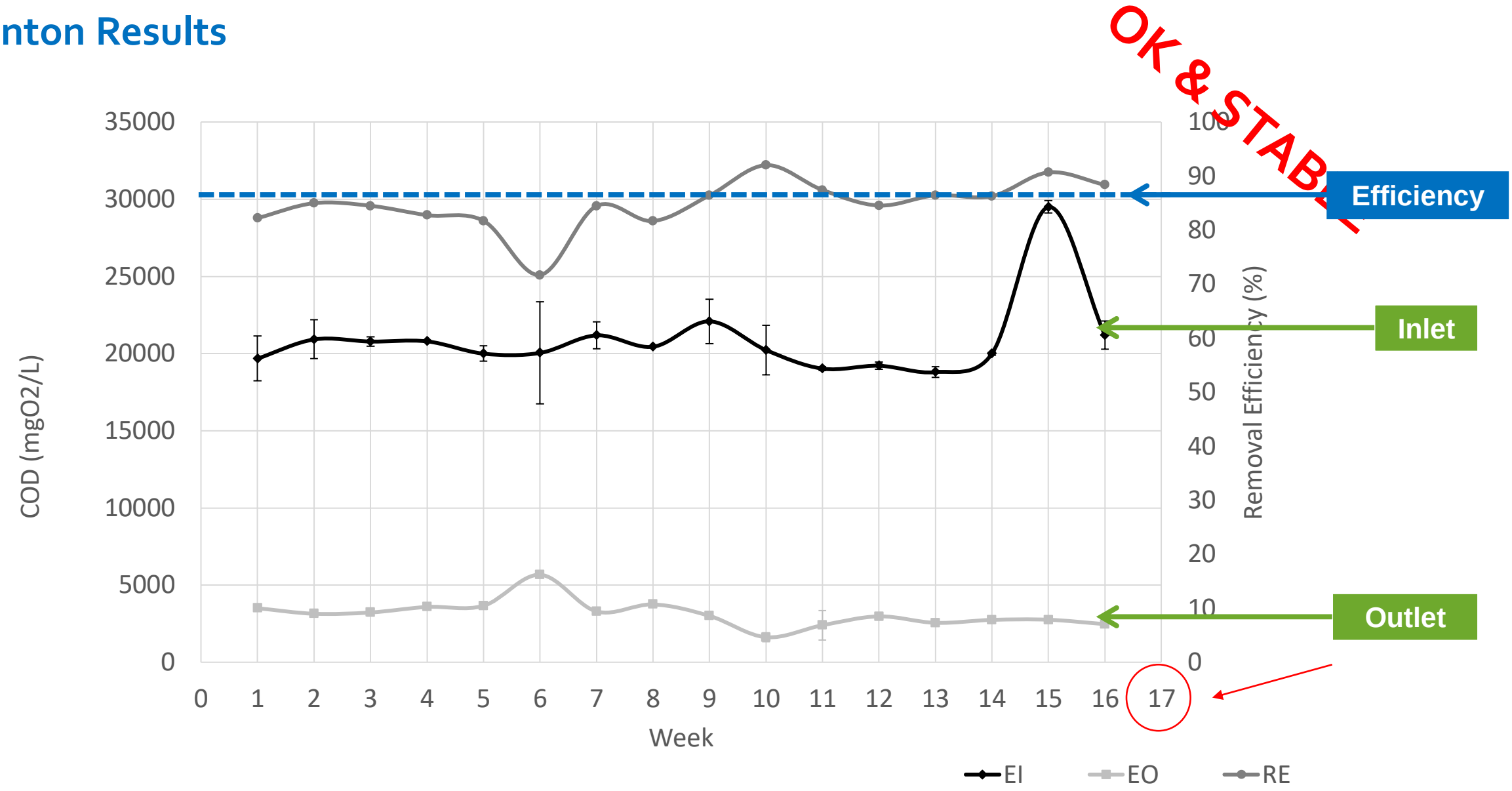
O_3

- Formation of foam (presence of foam agents such as detergents)

FENTON

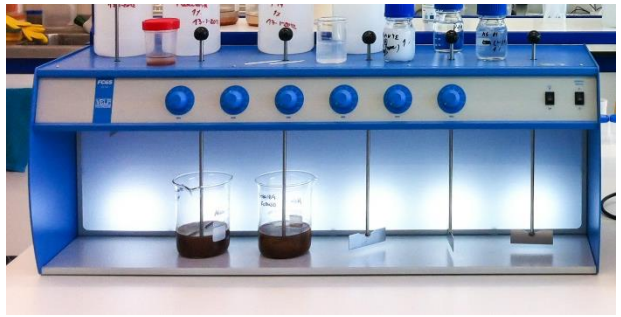
- Scavengers compounds

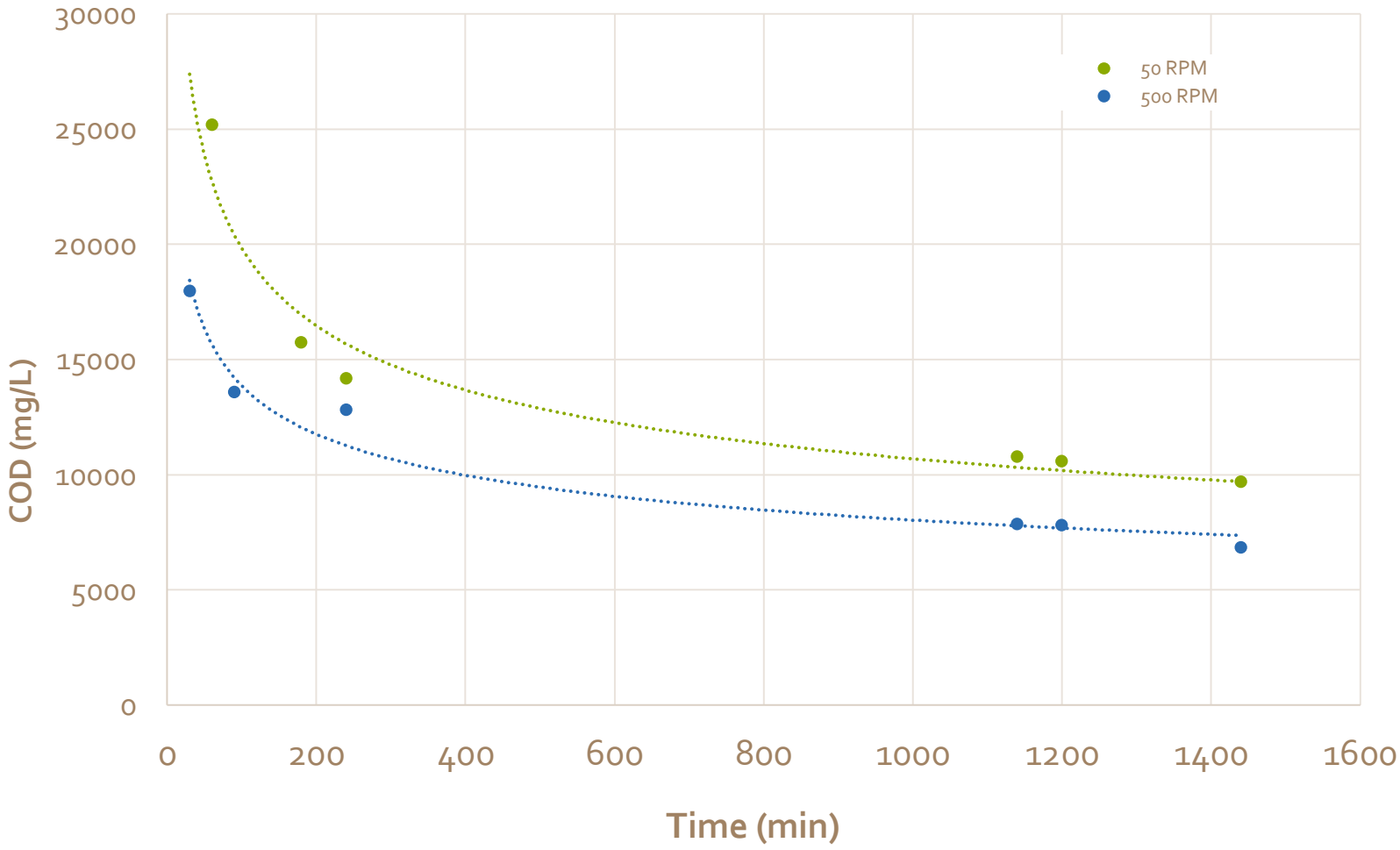
Fenton Results



Stirring Effect on Fenton Efficiency

$Fe_2SO_4.7H_2O$=		6	g/l
H_2O_2 50% =		8	ml/l
V= 400	mL		
pH= 3			





FENTON REACTOR SCALE-UP

IMPORTANT CONSIDERATIONS

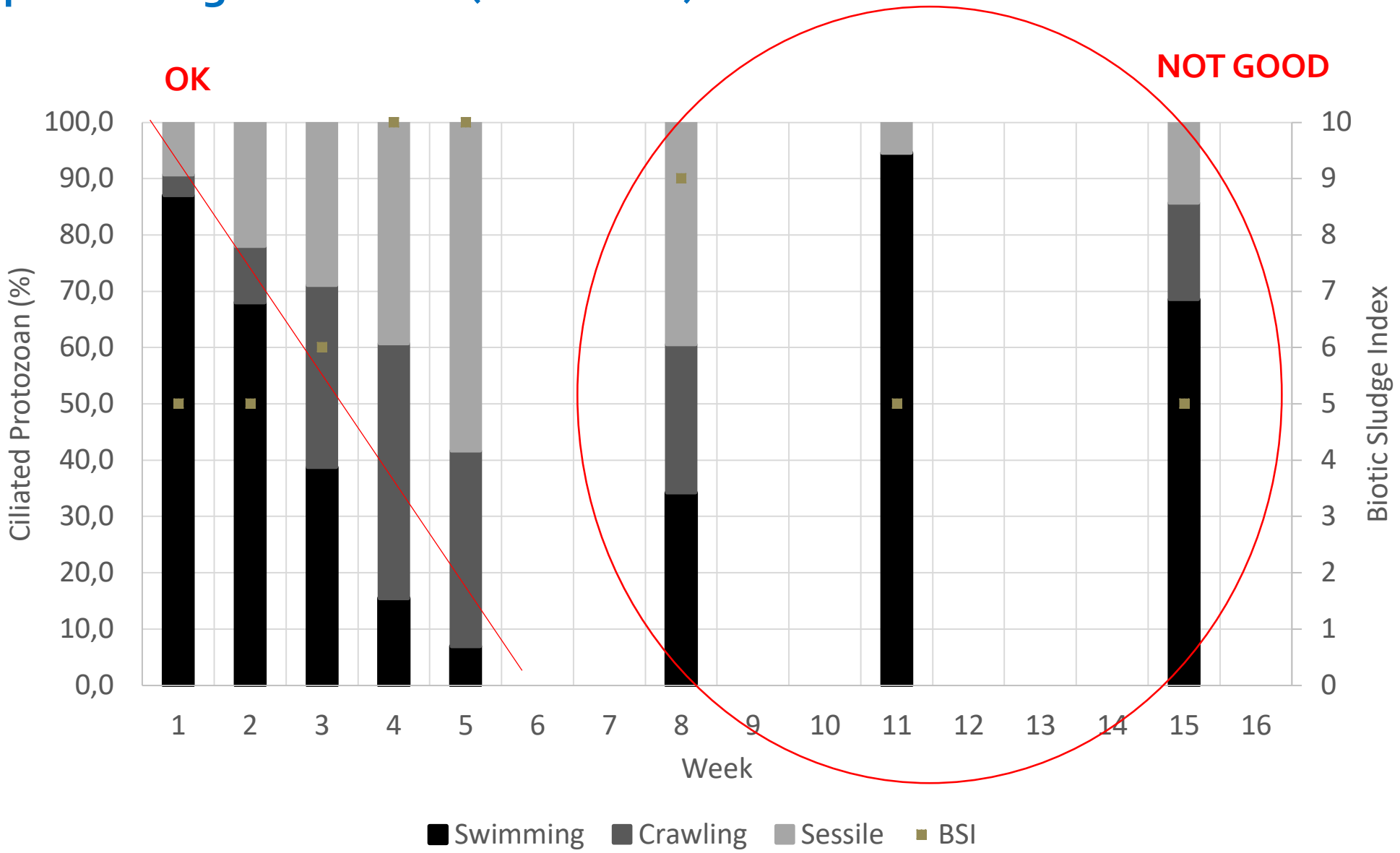
IN LAB TESTS		ON INDUSTRIAL REACTOR
Chemicals Doses	→	Use same. Adjust on Start-up.
Chemicals Dosing	→	Careful! Study effect of long dosing. Instantaneous dosing not possible on industrial plant.
Stirring	→	Main Problem. Consider at least more 30% Retention Time.
Materials	→	Problem. ***Fe*** on materials react!! Severe corrosion.

Sludge Removal

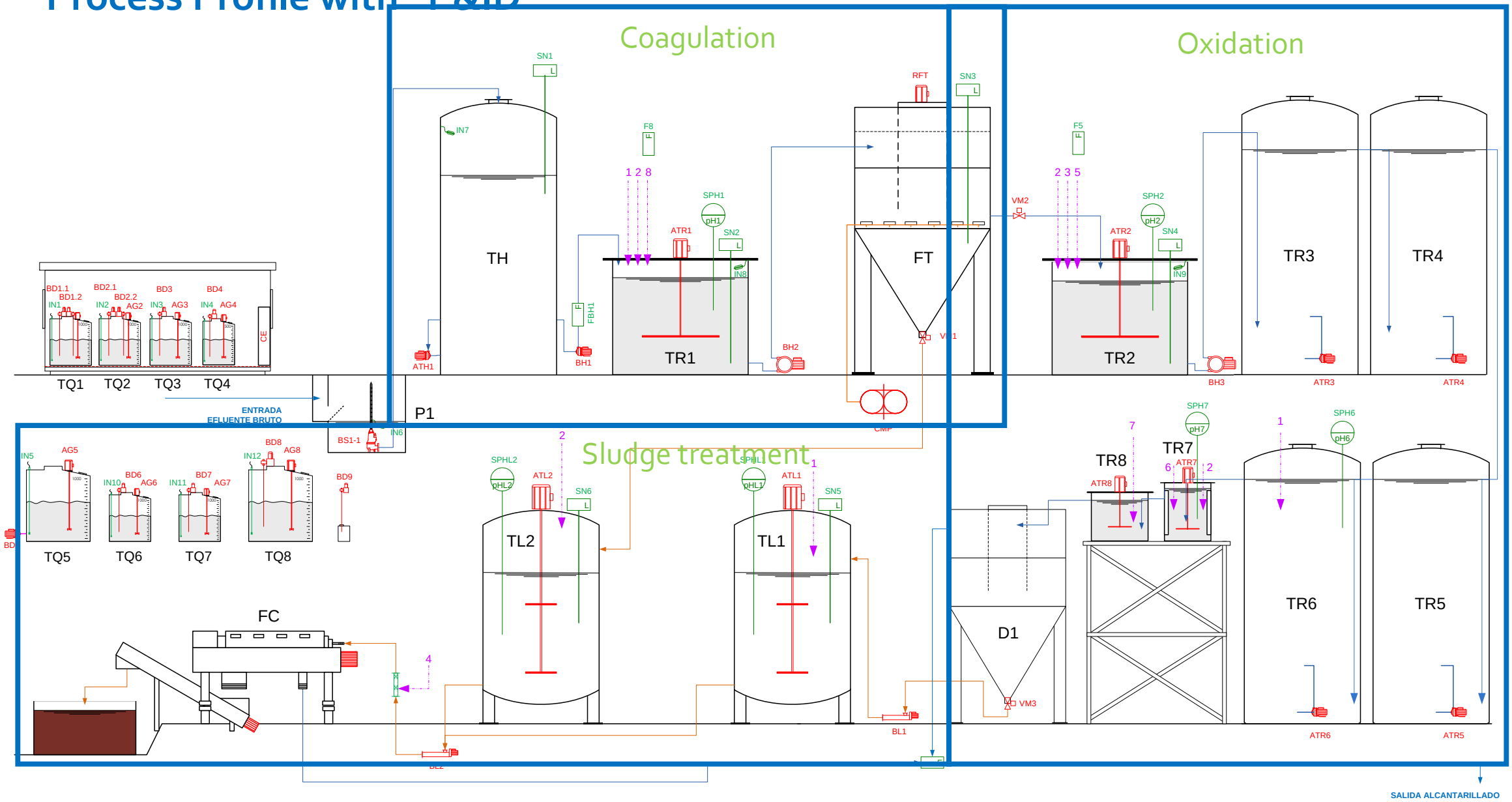
Coupled Biological Process (After AOP)

UNSTABLE

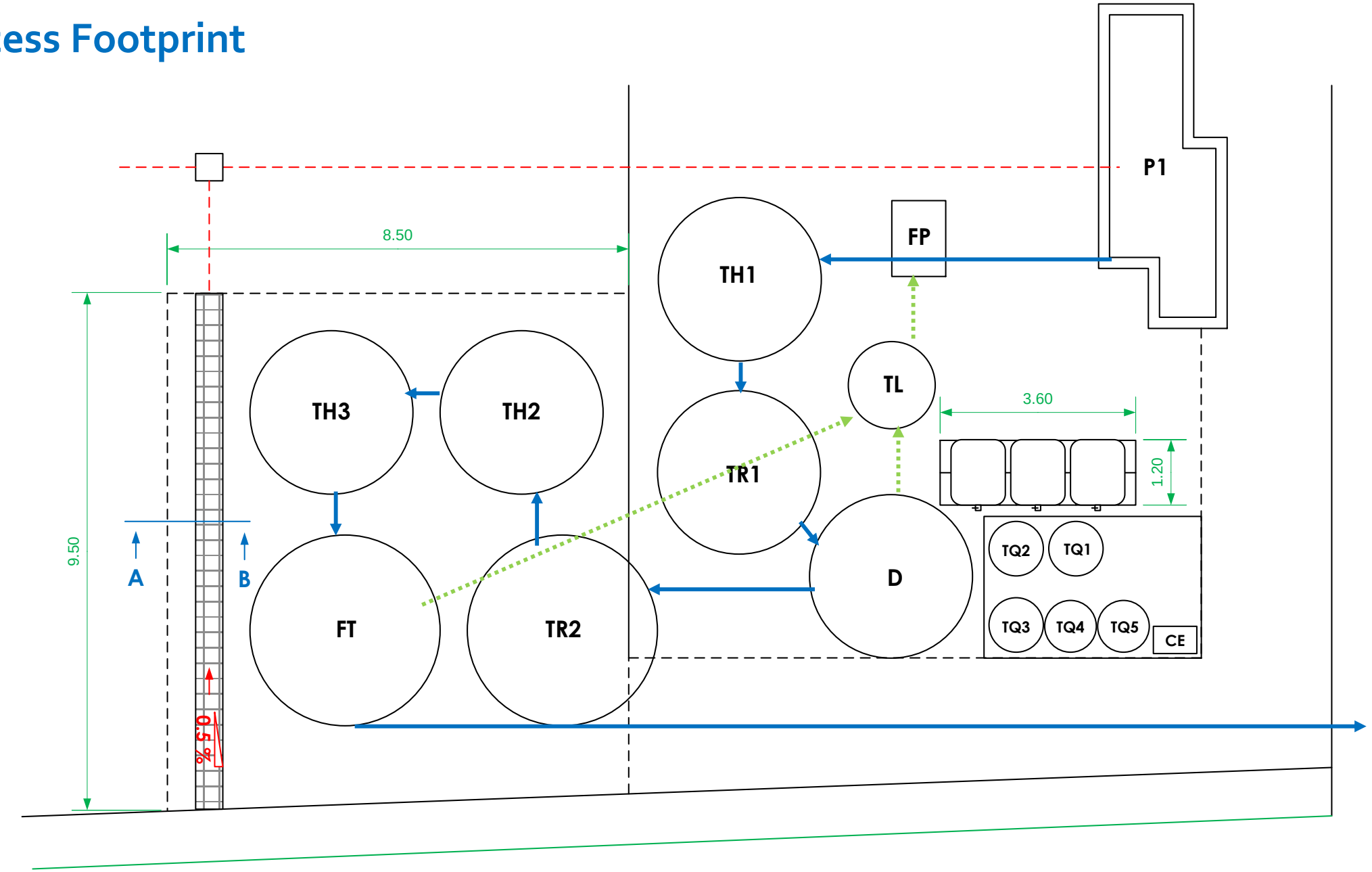
Coupled Biological Process (After AOP)



Process Profile with "P&ID"



Process Footprint



Final Plant Scale-Up

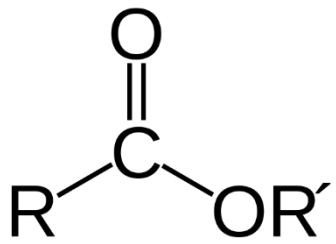
O3 SCALE-UP (Cases 3) – Rubber Pipe Industry

MAIN CHARACTERISTICS

- Low Turbidity (58 NTU)
- Some Detergents
- Low solids content
- Small daily quantity of Wastewater to treat (5 m3/d)
- Co (COD) = 6.000 – 10.000 mg O2/L
- C_{limit} (COD) = 150 mg O2/L

Main Chemical Compounds

DEMOULDING AGENTS

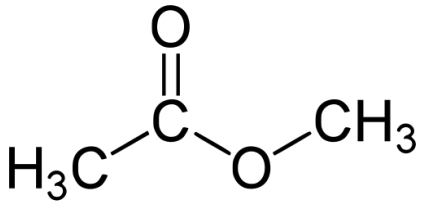


“Synthetic Oils”
(Ester’s)

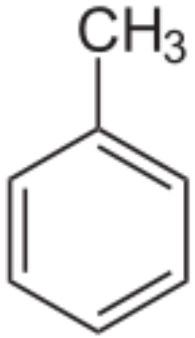
+

???
(surfactant’s)

SOLVENTS

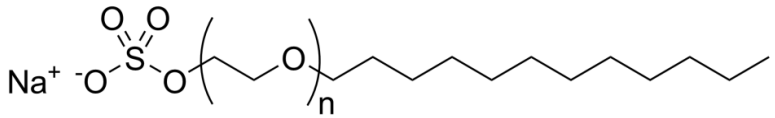


Methyl acetate
(Solvent)



Toluene
(Solvent)

CLEANERS

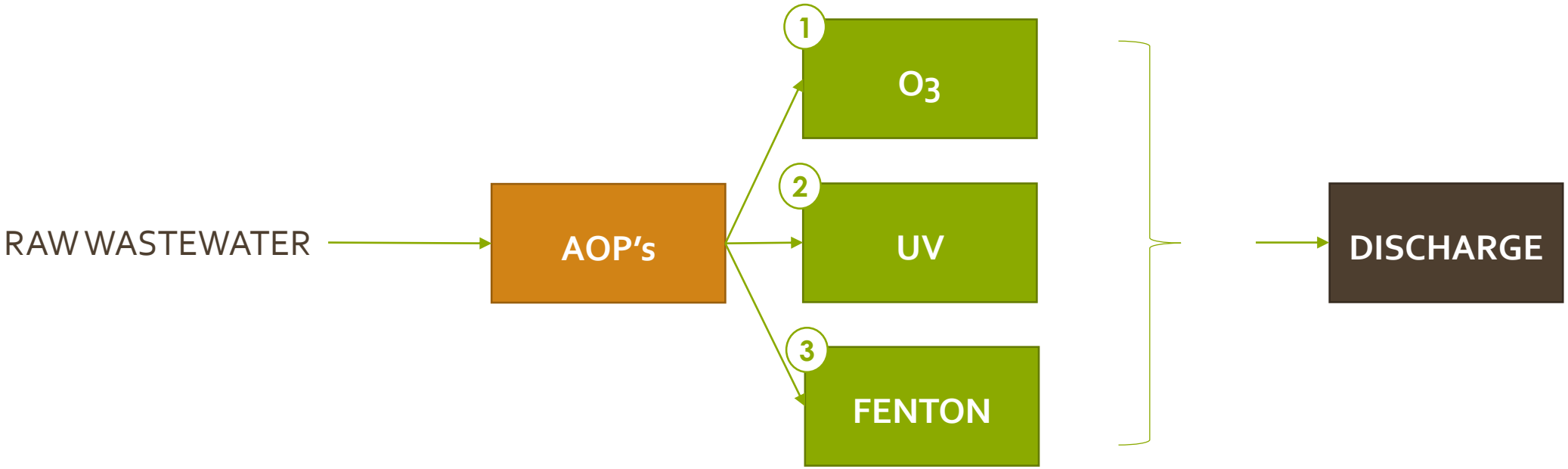


Sodium laureth sulfate
(Anionic Surfactant)

$$R - CH_2 - O - (CH_2 - CH_2 - O)_9 - H$$
$$R = C_{10}H_{21} \text{ or } C_{12}H_{25} \text{ (branched)}$$

Fatty Alcohol polyethylenglycol ether
(Nonionic Surfactant)

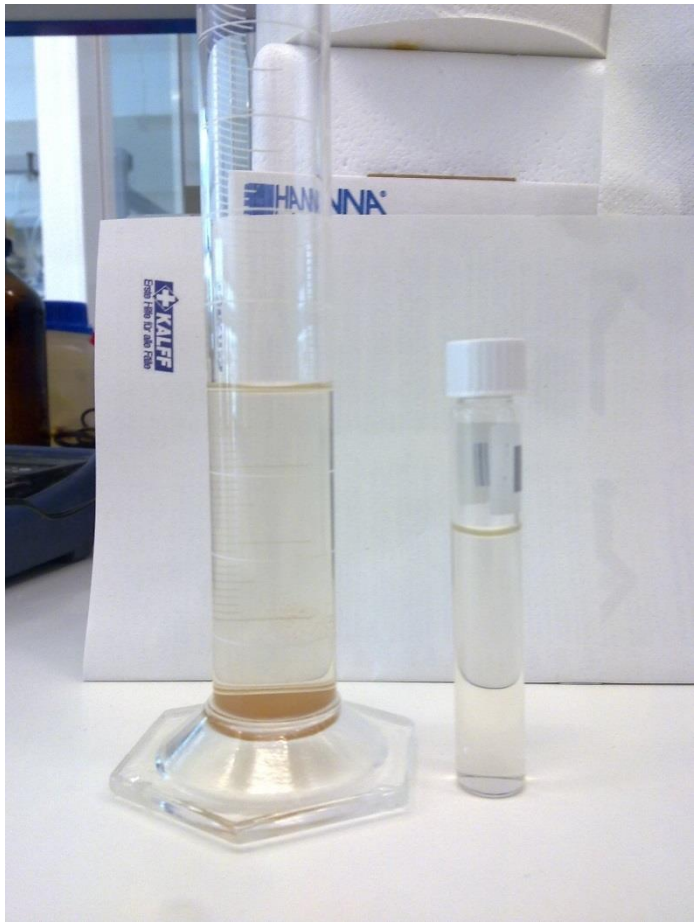
Lab Test Planning (CASE 3)



O3 – Lab Tests - Pilot

O3 – Lab Tests Results – Stages of Treatment

STAGES	pH
Initial	7,8
1st Stage Direct Oxidation (300 min) - Foam Removal - Decolouring - COD Removal: 27.5%	3
2nd Stage Radical Oxidation (900 min) - COD Removal: 70-75%	10
Neutralization	7-9

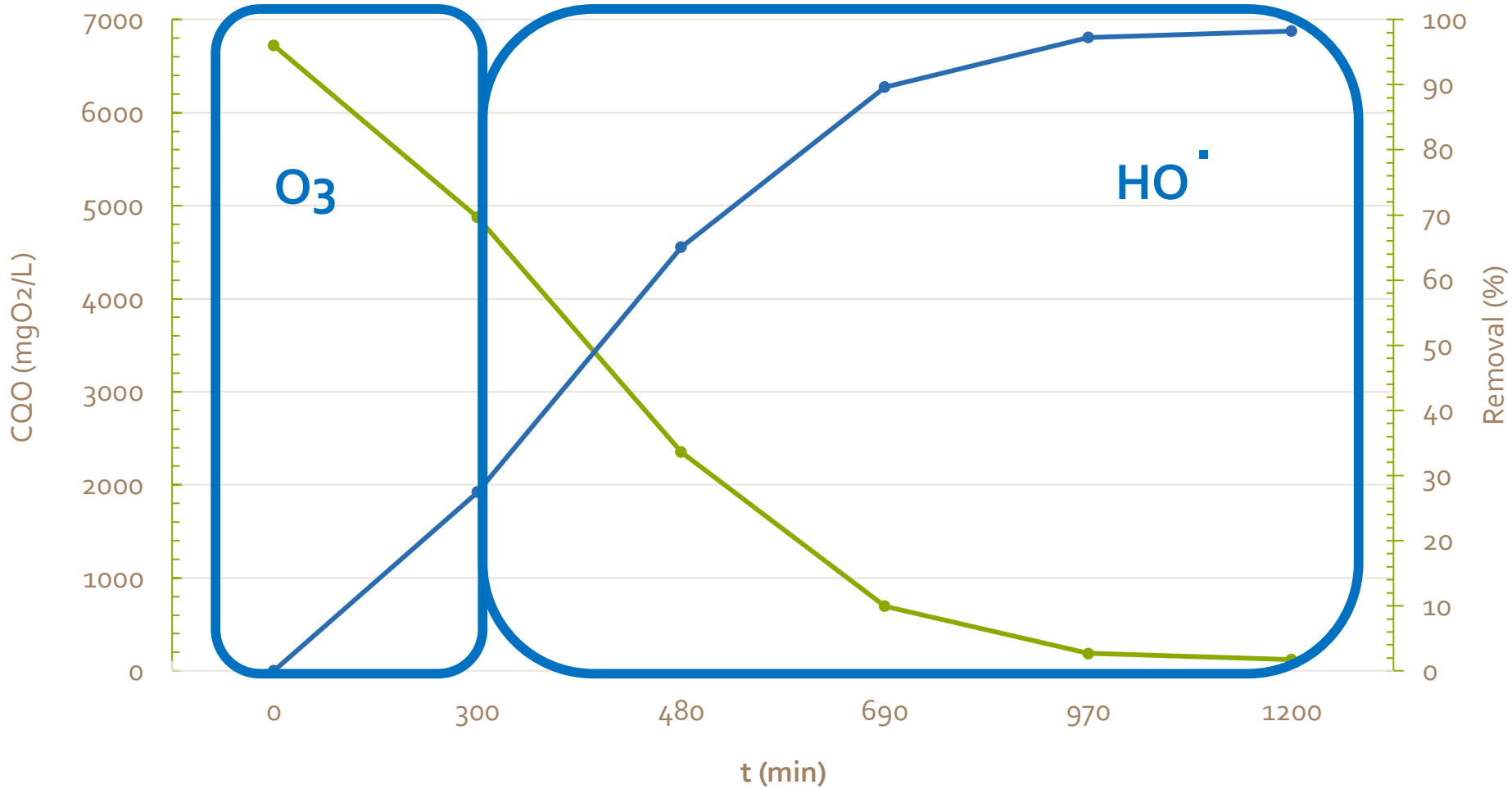


O3 – Lab Tests Results

		min			L/m3		mgO2/L	
	pHi	Time		pHf	H2SO4	NaOH	COD	% removal
--	9.12	0	0	--	--	--	6720	0
O3 (3)	3.1	300	300	2.56	3.5	--	4873	27.5
O3 (10)	10.6	180	480	8.2		2.8	2350	65.0
O3 (10)	10.7	210	690	10.6		3.6	696	89.6
O3 (10)	10.7	280	970	11.1		2.8	188	97.2
O3 (10)	11.1	230	1200	10.9	--	--	122	98.2
Total		1200			7.5	9.2		
Detergents								<1 mg

O3 consumed in the reaction = 200 g / m3

O3 – Lab Tests Results



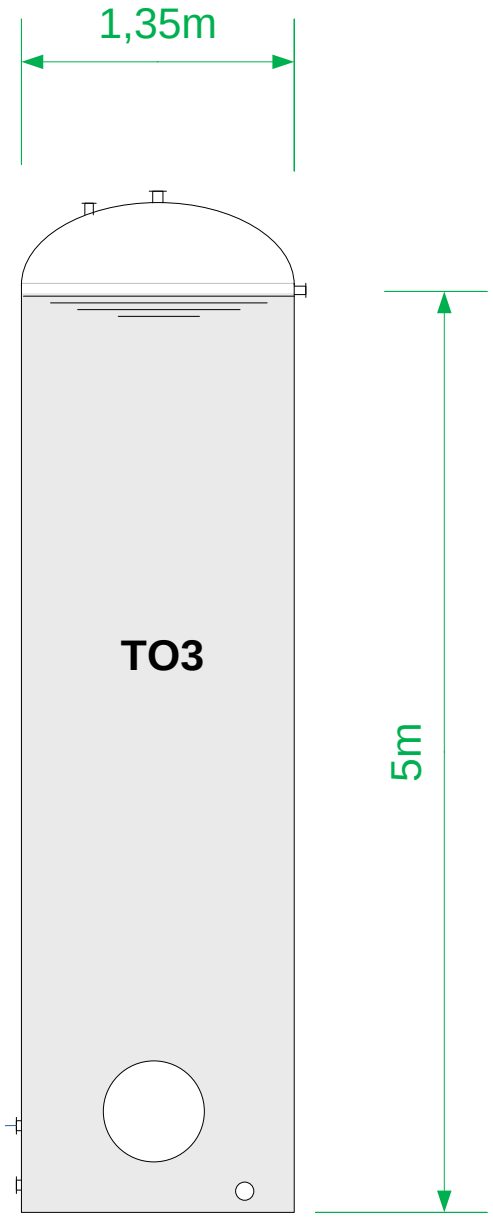
O_3 – DATA FOR SCALE-UP

DATA OBTAINED

O_3 = 200 g/m3 ➡ Q = 5 m3/day ➡ O_3 (total) = 1 kg /day

SCALE-UP

- Cost effective commercial ozone generator with air feed : 60 g O_3 / h
  (limit 200 g O_3 / h)
- Max. efficiency of fine bubble diffusion on water between 4 – 6 m water column
- HRT = 1 day
- Total O_3 = 60 x 24 = 1440 g/day
- Ozone injection by medium-pressure vertical pump & venturi



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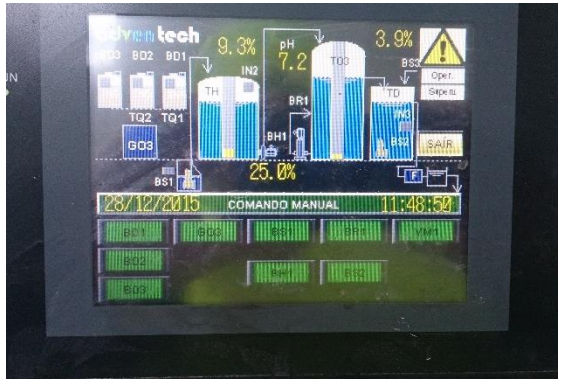


Final Plant Scale-Up

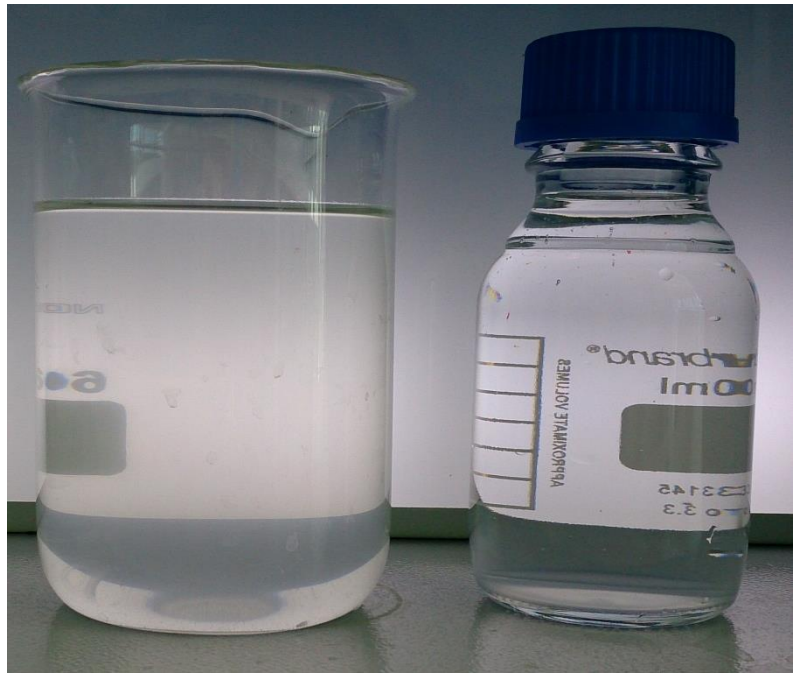
O_3 REACTOR SCALE-UP

IMPORTANT CONSIDERATIONS

IN LAB TESTS		ON INDUSTRIAL REACTOR
O_3	→	Use + 30-40%
O_3 Dosing	→	Careful! In Column if possible. Injection system have big influence. Use large HRT for minimize O_3 Generator cost.
pH	→	Always monitor pH
Materials	→	Problem. O_3 leaks.
Safety	→	Don't forget O_3 destroyer and O_3 ambient monitor.

UV SCALE-UP (Cases 5) – Bio Fungicide

- 360 m3/day
- Process Water
- Re-use on Hydroponics
- TBC at 37°C = 1 x 10^5 cfu/mL
- Coliform = 5 x 10^2 N/100 mL
- E.Coli > 100 N/100mL
- TARGET = 0



UV REACTOR SCALE-UP

IMPORTANT CONSIDERATIONS

IN LAB TESTS		ON INDUSTRIAL REACTOR
UV	→	Use same wavelength. More + 25% power .
UV Dosing	→	Measure applied Light (Photons - Chemical Actinometry).
Installation	→	Shell Tube Inline or Multiple Lamps submerged in a tank.
Material	→	Stainless Steel

Conclusions:

- Use of AOP coupled with conventional technologies;
- Scale-Up needs a correction factor;
- The operational costs are mandatory to the AOP's application.

AOP's SUMMER SCOOL

10 - 14 July 2017, Porto, Portugal

From bench to full scale AOP's application

S. Castro-Silva, Adventech, Portugal