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Overcome Barriers in the Treatment of Leachates from Urban Solid Waste Landfills: from Lab to Industrial Studies

AOPs PhD School

1st Summer School on *Environmental Applications of Advanced Oxidation Processes*

University of Salerno

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LABORATÓRIO ASSOCIADO
LSRE
LCM

Associate Laboratory LSRE/LCM

Shaking the Present, Shaping the Future

Abanando o presente, formatando o futuro

http://lsre.fe.up.pt/

Associate Laboratory

Laboratory of Separation and Reaction Engineering
Laboratório de Processos de Separação e Reacção
Director: Alírio Rodrigues

Laboratory of Catalysis and Materials
Laboratório de Catálise e Materiais
Director: José Luís Figueiredo

FEUP - Faculdade de Engenharia da Universidade do Porto
DEQ - Departamento de Engenharia Química

UP - Universidade do Porto

Research Areas

I - Cyclic Adsorption/Reaction Processes

IA- Cyclic Adsorptive Processes

IB- Process Intensification/Multifunctional Reactors

II - Product Engineering

IIA- Perfume Engineering & Microencapsulation

IIB- Aroma Chemicals and Drug Precursors

IIC- Chemical Reaction and Polymer Engineering

III - Environmental Science and Engineering

IIIA- Aquatic Systems

IIIB- Processes for Pollution Control

IV - Chemical Engineering Thermodynamics

IVA- Separations in Aqueous Media

IVB- Enzymatic Processes in Non-Aqueous Media

IVC- Molecular Modelling and Molecular Simulation

V - Catalysis and Materials

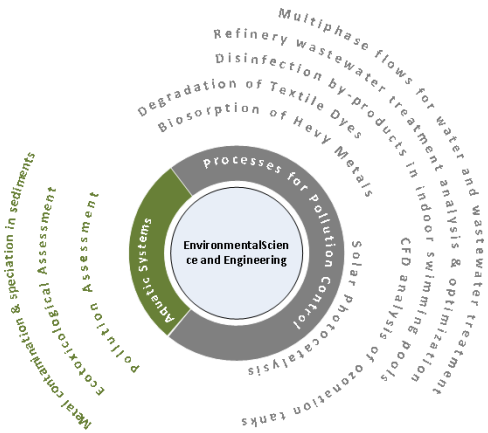
VA- Nanostructured Carbon Materials and Catalysts

VB- Environmental Catalysis and Related Technologies

VC- Catalytic Technologies for Sustainability

Research Areas

- **Aquatic Systems**
  - Environmental Assessment and Monitoring of Surface Waters
  - Hydrologic Modelling Using HSPF
  - Water Quality Modelling Using BASINS Watershed Tool (Better Assessment Science Integrating Point & Non-Point Sources)
- **Processes for Pollution Control**
  - Use of Environmental Friendly Technologies for Water and Air Decontamination
    - Biological Oxidation Processes
    - Sorption/Biosorption using Natural Materials
    - Solar Driven Advanced Oxidation Processes
    - Solar Driven Electrochemical Oxidation Processes
    - Combination of Physical, Biological, Chemical and Membrane Processes
  - Wastes Valorization for Methane Production by Anaerobic Digestion



Solar Driven AOPs Research Team

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Maria Francisca da Costa Moreira
André Almeida Nogueira
Belisa Alcântara Marinho
Jonathan Cawettiere Almeida Espíndola

Research fellowships
Eloísa Sofia da Silva Vieira

SOLAR WATER DECONTAMINATION

SOLAR WASTEWATER DECONTAMINATION

SOLAR AIR DECONTAMINATION

Solar Driven AOPs Research Topics

Elimination of Emerging Pollutants from Water and Wastewaters using Solar Advanced Oxidation Processes

Water
- Microorganisms
- Oxanions
- Cyanobacteria
  - Cyanotoxins

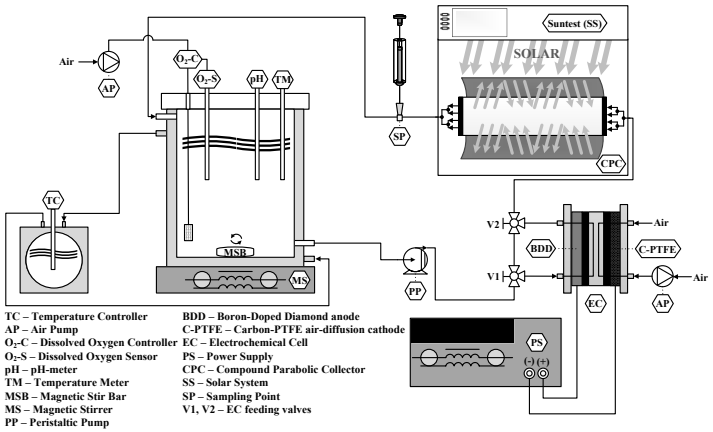
Domestic Wastewater Reuse
- Emergent Pollutants
  - Pharmaceutical
  - Antibiotics
  - Fragrances

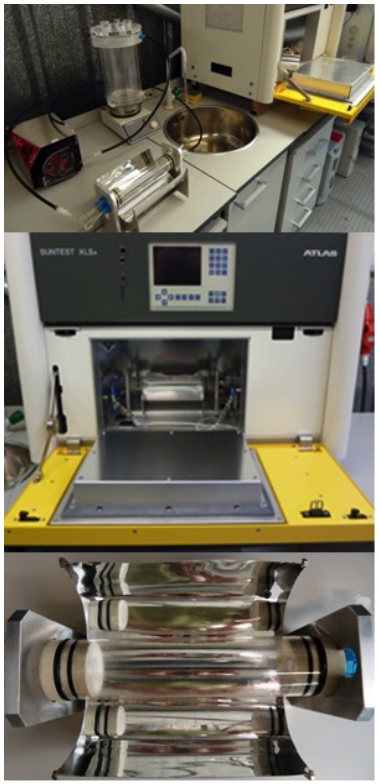
AOPs
- Fenton
- Solar/Artificial Photo-Fenton
- TiO_2 or TiO_2/H_2O_2 Photocatalysis
  - Homogeneous
  - Heterogeneous
- TiO_2 Photocatalytic Paints

EAOPs
- Anodic Oxidation with Electrogeneration of H_2O_2
- Electro-Fenton (EF)
- PEF and SPEF

Autonomous Pilot Plant With CPCs

AOPs/EAOPs Lab-Scale Prototype





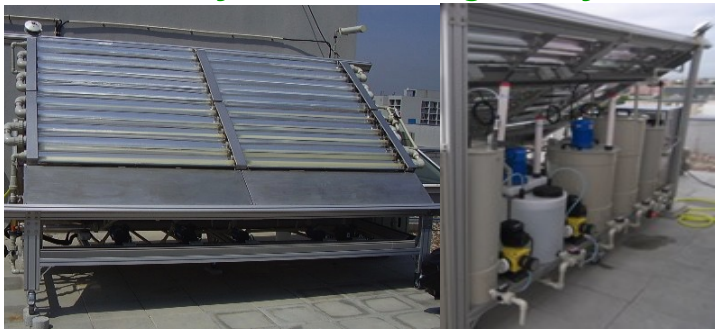
Solar Driven AOPs Research Topics

Treatment of Industrial Wastewaters using Combined Chemical and Biological Oxidation Processes

Industrial Wastewaters

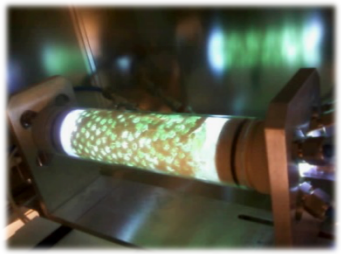
- Landfill Leachates
- Textile
- Cork Boiling and Bleaching
- Pharmaceutical
- Aquaculture
- Pesticides
- Winery

Solar Pilot Plant with a Combined Photocatalytic and Biological System



Pre-Industrial Plant-Leachates

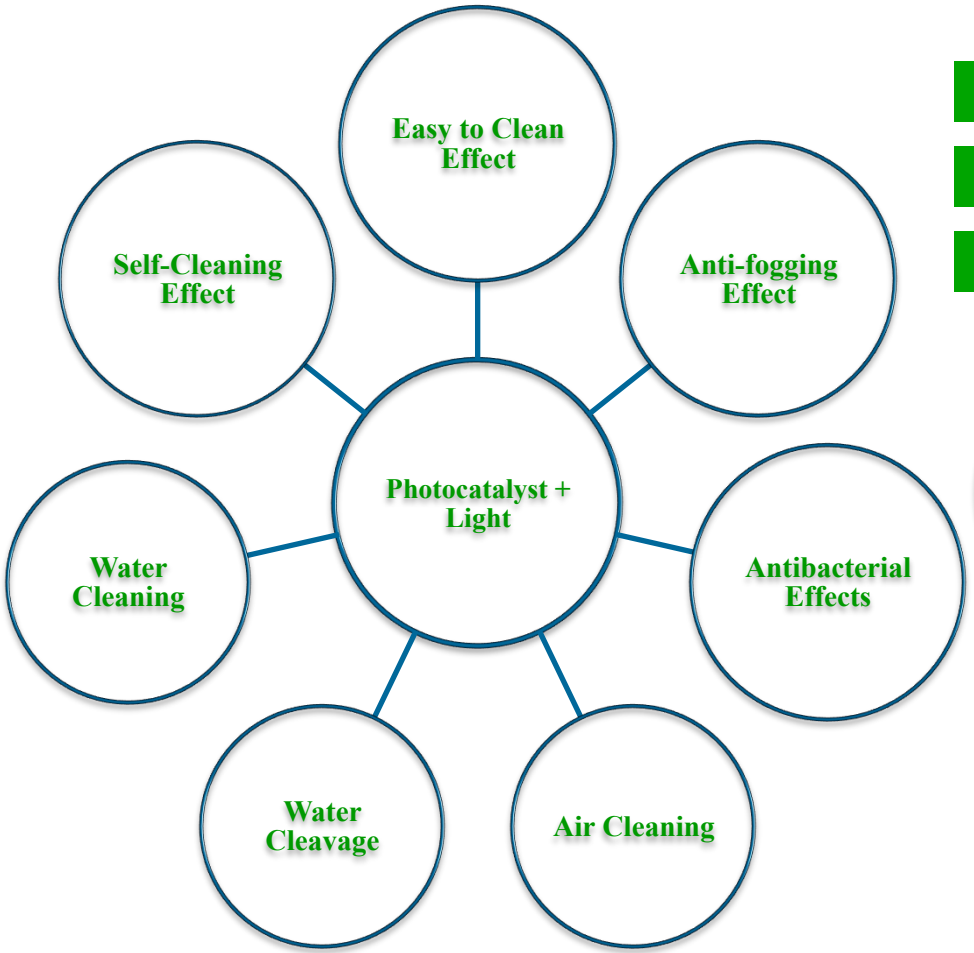
Indoor Air Decontamination using Heterogeneous Solar Photocatalytic Processes (VOCs and Microorganisms)

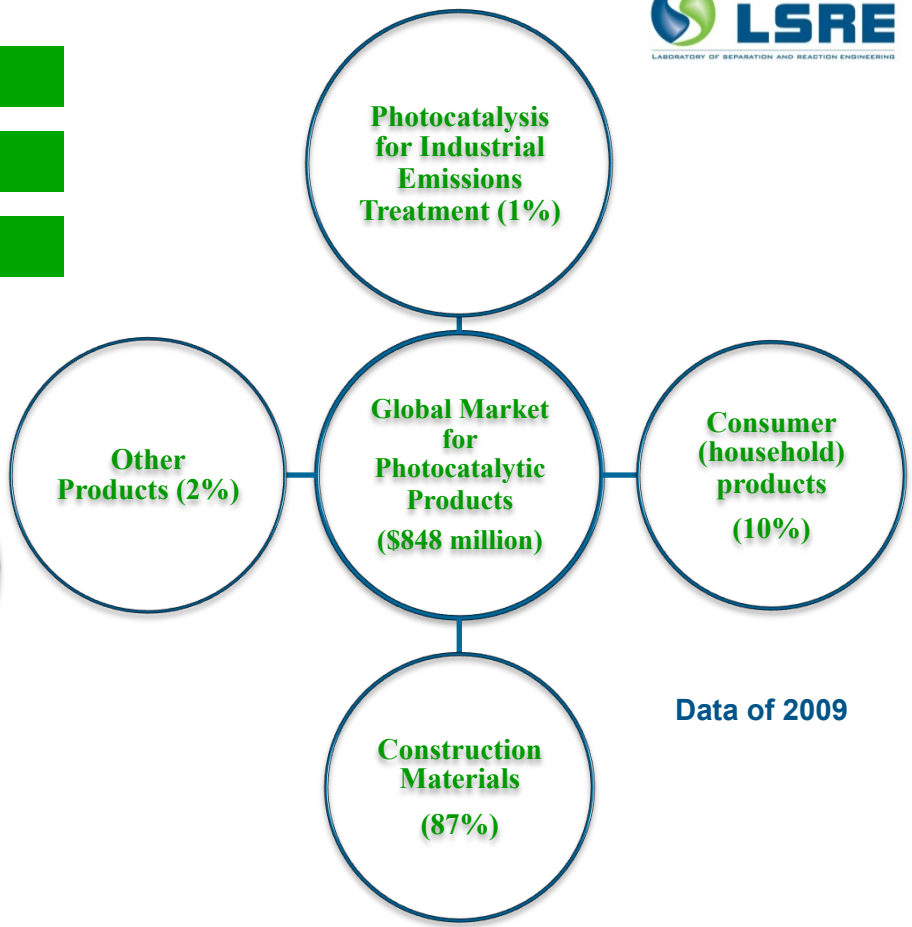


Lab-Scale Continuous Flow Tubular Photoreactor

Pilot-Scale Continuous Flow Tubular Photoreactor with CPCs

Applications of Photocatalysis/Market





Data of 2009

ObservatoryNANO, Briefing nº.10, Chemistry & Materials, Application of Photocatalysis, February 2011

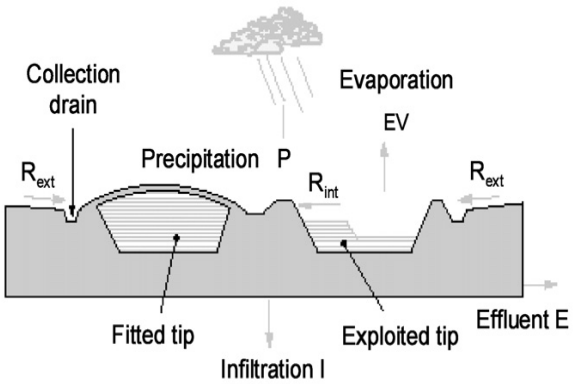
Despite the Potential for this Clean Technology for those Emissions, it has Not Reached a Mature Level for Out-of-Niche Applications

Outline

- Leachate from Sanitary Landfills;
- Multistage Treatment System for Mature Leachates;
  - From Lab-Scale to Industrial Scale;
  - Prototypes;
  - Nitrogen Removal by Activated Sludge Biological Treatment
    - Nitrification Reaction
    - Denitrification Reaction
- Conclusions

Leachate from Sanitary Landfills

WATER CYCLE IN SANITARY LANDFILLS



H. Billard, Centre de stockage des d´echets Exploitation, 2001.

LANDFILL LEACHATE CLASSIFICATION vs. AGE

	RECENT	INTERMEDIATE	OLD
AGE (YEARS)	< 5	5 - 10	> 10
pH	< 6.5	6.5 – 7.5	>7.5
COD (mg L^{-1})	> 10000	4000 - 10000	< 4000
BOD_5/COD	> 0,3	0.1 – 0.3	< 0.1
ORGANIC COMPOUNDS	80 % VOLATILE FAT ACIDS (VFA)	5 – 30% VFA + HUMIC AND FULVIC ACIDS	HUMIC AND FULVIC ACIDS
HEAVY METAL	LOW – MEDIUM	-	LOW
BIODEGRADABILITY	IMPORTANT	MEDIUM	LOW

E.S.K. Chian, F.B. DeWalle, J. Environ. Eng. Div. (1976) 411–431.

Multistage Treatment System For Leachates

Leachate Treatment Plant at Sanitary Landfill

Raw Leachate
(150 m³/day)

Aerated Lagoon
(15,000 m³)

Anoxic and Aerobic Activated Sludge Reactors
(150 m³ each)

Coagulation/Flocculation System

Retention Lagoon
(3000 m³)

Treated Leachate

Transported to a municipal WWTP, since it does **not meet** the **discharge regulations** into **sewerage systems** and **water bodies**

Leachate used in the tests

Leachate Treatment Strategy used at Pre-Industrial scale

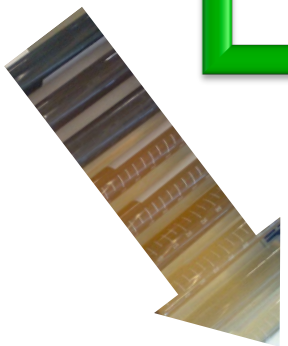
European Patent nr. 14161588.0

Biological Oxidation
(under aerobic conditions)

Coagulation Sedimentation

Photo-Oxidation
(photo-Fenton reaction)

Biological Oxidation
(under aerobic and anoxic conditions)



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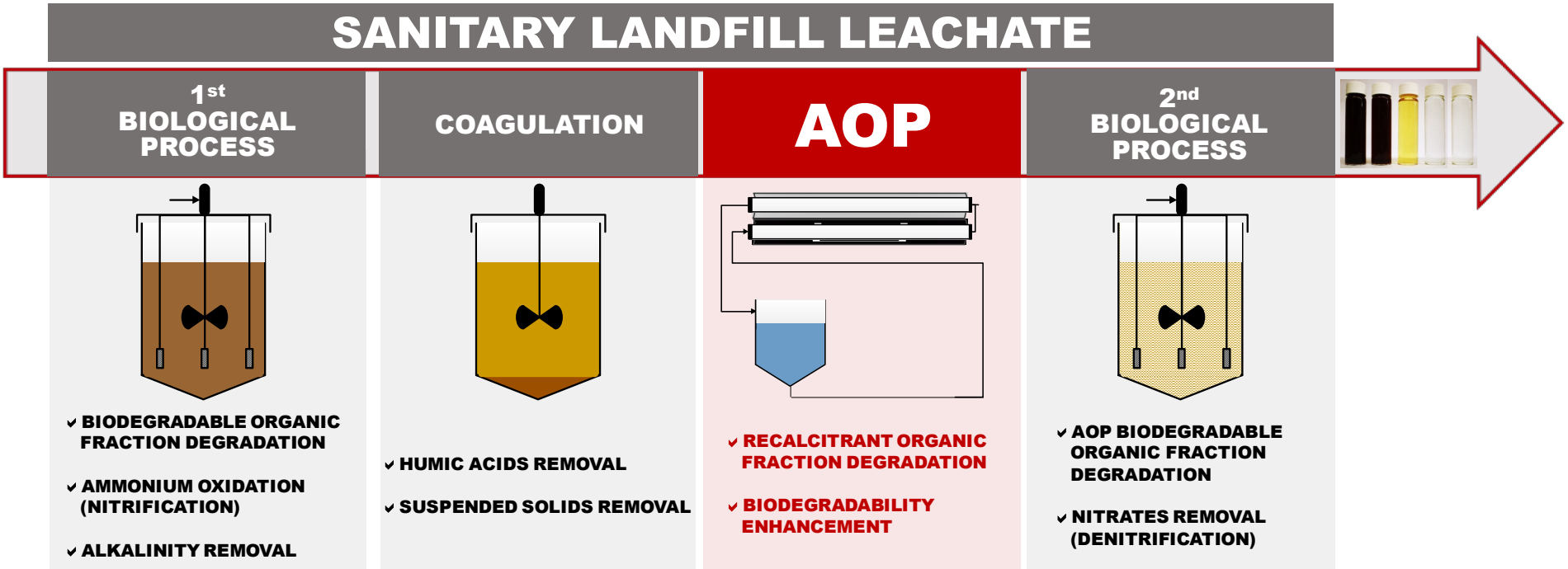
Multistage Treatment System For Leachates



European Patent nr. 14161588.0

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Faculdade de Engenharia
FEUP

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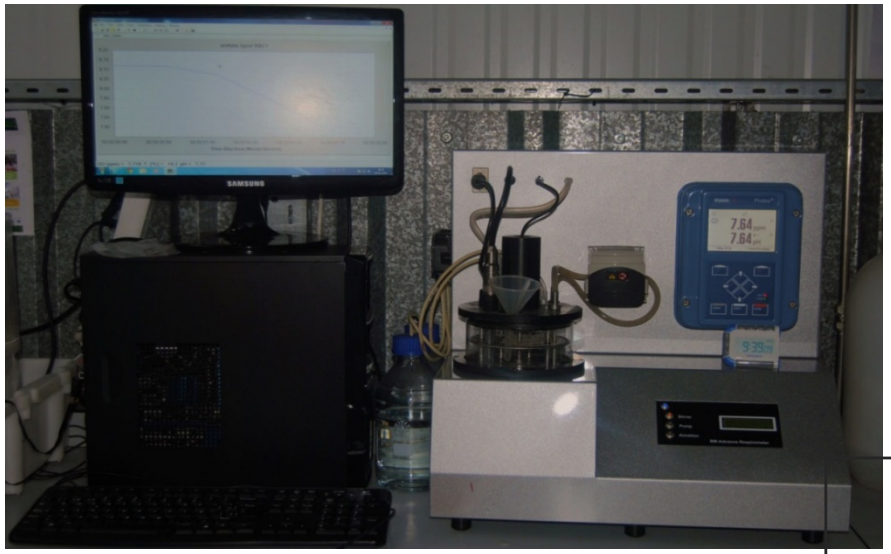
Title: Method of Treating Leachate, Phototreatment Reactors and Respective Use

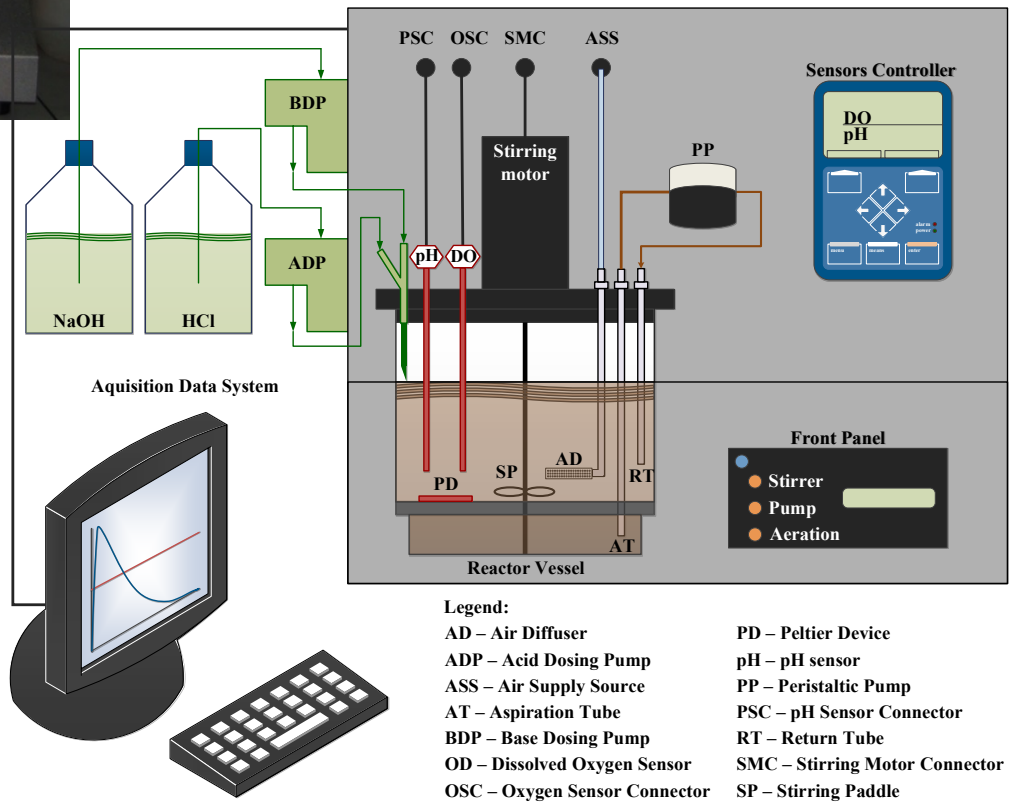
Applicant: EFACEC ENGENHARIA E SISTEMAS, S.A.

Authors: Isabel Maria Alexandre Saraiva, Maria Amélia Ferreira da Fonseca, Tânia Filomena Castro Valente Silva, Rui Alfredo da Rocha Boaventura, Vítor Jorge Pais Vilar

Lab-Scale-Biological Oxidation



Respirometer



Legend:

AD – Air Diffuser
ADP – Acid Dosing Pump
ASS – Air Supply Source
AT – Aspiration Tube
BDP – Base Dosing Pump
OD – Dissolved Oxygen Sensor
OSC – Oxygen Sensor Connector
PD – Peltier Device
pH – pH sensor
PP – Peristaltic Pump
PSC – pH Sensor Connector
RT – Return Tube
SMC – Stirring Motor Connector
SP – Stirring Paddle

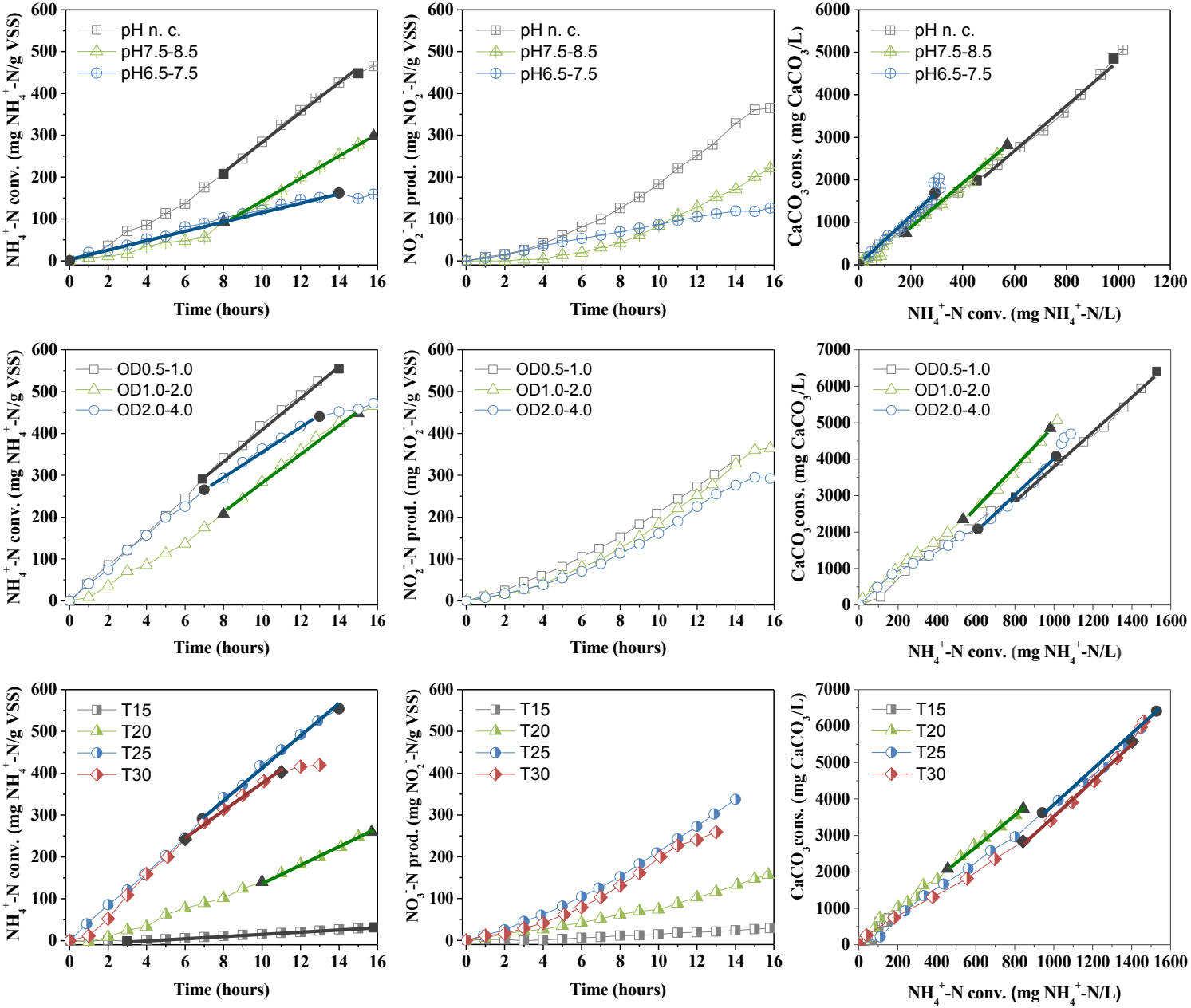
Lab-Scale-Biological Oxidation

Nitrification

Stoichiometric ratio: 7.14

Group	pH range	pH_m	DO range (mg/L)	DOa (mg/L)	T (ºC)	VSS (g/L)	NH_4^+-N_{AS} (%)	$k_{nit.}$ $\left(\frac{mg\ NH_4^+-N}{g\ VSS.h}\right)$	Alkalinity $\left(\frac{mg\ CaCO_3}{mg\ NH_4^+-N}\right)$
I Effect of pH	Not controlled	8.73	1.0-2.0	1.35	25	2.19	20.3	35±2	5.4±0.4
	7.5-8.5	8.18		1.26		1.92	14.6	27±1	5.1±0.3
	6.5-7.5	7.02		1.83		1.94	6.4	11.6±0.4	5.5±0.2
Effect of DO	Not controlled	8.75	0.5-1.0	0.53	25	2.76	34.3	38±2	4.6±0.3
		8.73	1.0-2.0	1.35		2.19	20.3	35±2	5.4±0.4
		8.91	2.0-4.0	3.07		2.30	38.0	30±2	4.9±0.4
Effect of Temperature	Not controlled	8.91	0.5-1.0	1.26	15	2.92	0.7	2.6±0.1	**4.0±0.7**
		8.92		0.99	20	3.25	22.5	21.3±0.7	4.1±0.2
		8.75		0.53	25	2.76	34.3	38±2	4.6±0.3
		8.59		0.41	30	3.48	38.1	32±2	4.9±0.4

Lab-Scale-Biological Oxidation



Biomass Inhibition for pH<7.0

Similar Behaviour

Biomass Inhibition for T<25ºC

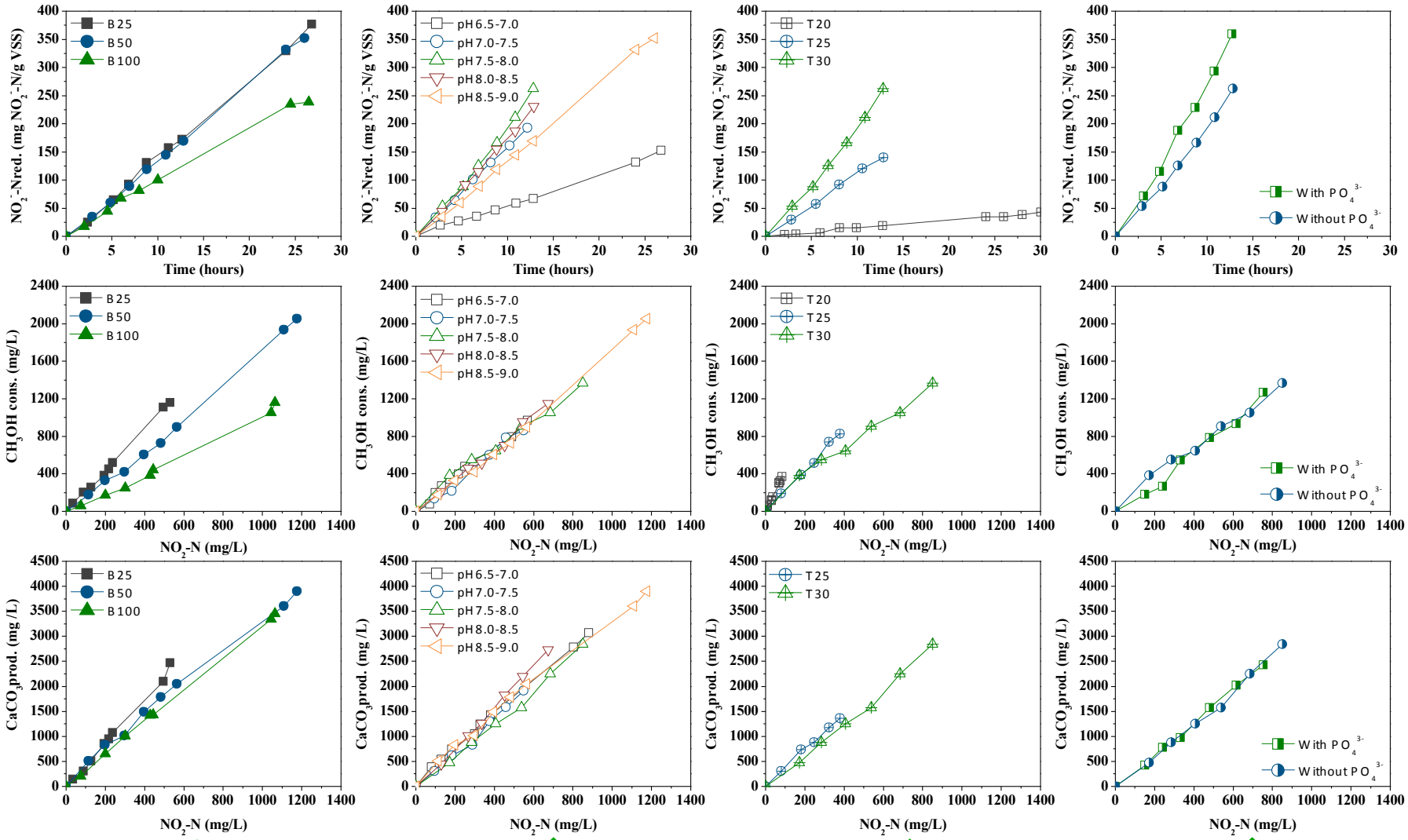
Lab-Scale-Biological Oxidation

Denitrification

Stoichiometric ratio: 1.53 3.57

Group	Biomass	pH range	pH_m	T (°C)	VSS (g/L)	$k_{desn.}$ $\left(\frac{mg\ NO_2\text{-}N}{g\ VSS.h}\right)$	Methanol $\left(\frac{mg\ CH_3OH}{mg\ NO_2\text{-}N}\right)$	Alkalinity $\left(\frac{mg\ CaCO_3}{mg\ NO_2\text{-}N}\right)$
I Effect of Biomass	25	8.5-9.0	8.90	30	1.38	13.9±0.3	2.18±0.05	4.4±0.1
	50		8.90		3.34	13.5±0.2	1.69±0.06	3.4±0.1
	100		8.82		4.46	9.4±0.3	1.02±0.05	3.23±0.03
II Effect of pH	50	6.5-7.0	6.77	30	3.72	5.5±0.1	1.72±0.08	3.5±0.1
		7.0-7.5	7.15		2.86	15.8±0.2	1.59±0.09	3.4±0.1
		7.5-8.0	7.86		3.24	19.4±0.7	1.63±0.09	3.2±0.1
		8.0-8.5	8.04		2.92	17.5±0.4	1.67±0.07	4.0±0.1
		8.5-9.0	8.90		3.34	13.5±0.2	1.69±0.06	3.4±0.1
III Effect of Temperature	50	7.5-8.0	7.42	20	2.00	1.4±0.1	4.3±0.2	---
			7.78	25	2.70	11.1±0.3	2.19±0.06	3.6±0.1
			7.86	30	3.24	19.4±0.7	1.63±0.09	3.2±0.1
IV Phosphate addition	50	7.5-8.0	7.86	30	3.24	19.4±0.7	1.63±0.09	3.2±0.1
			7.85		**2.10**	**27±1**	**1.6±0.1**	**3.2±0.1**

Lab-Scale-Biological Oxidation



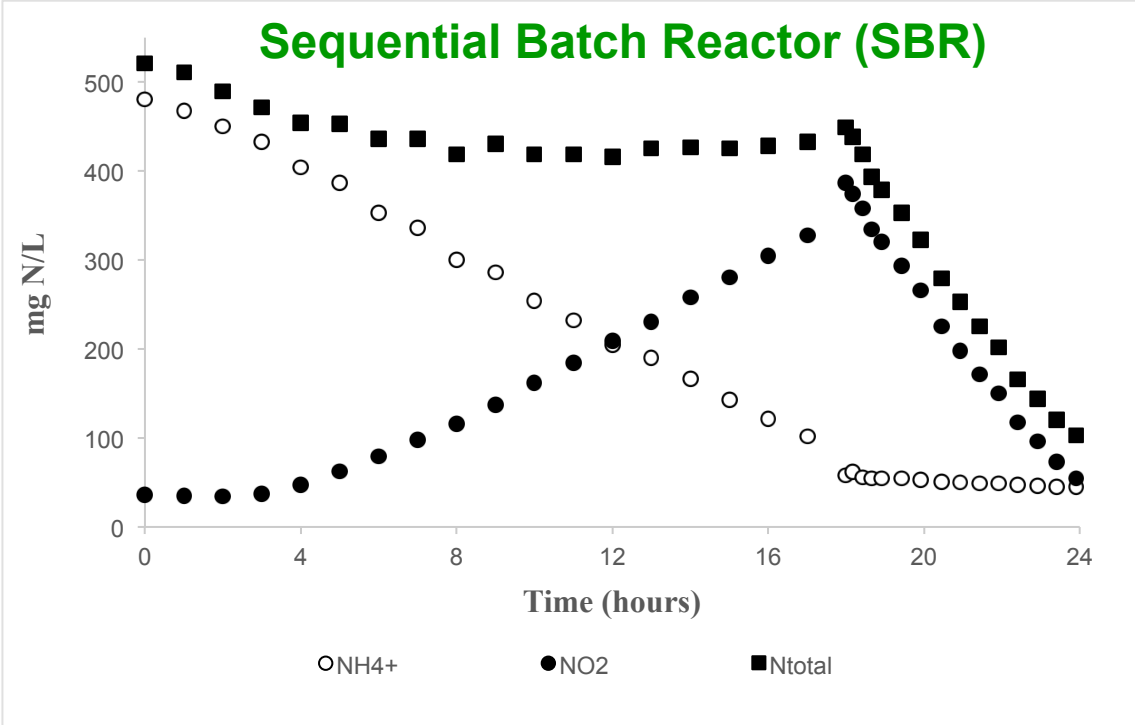
Low Denitrification Rates for VSS>3.5 g/L

Biomass Inhibition for pH<7.0 and pH>8.5

Biomass Inhibition for T<25ºC

Phosphate Addition Enhances Denitrification

Pilot-Scale-Biological Oxidation

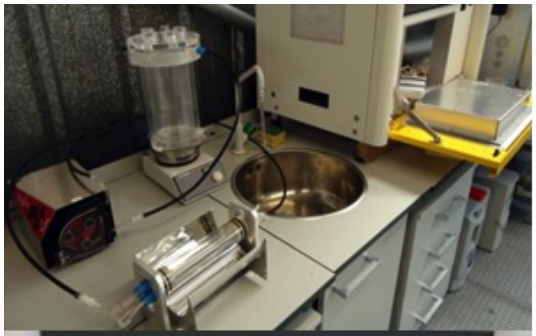


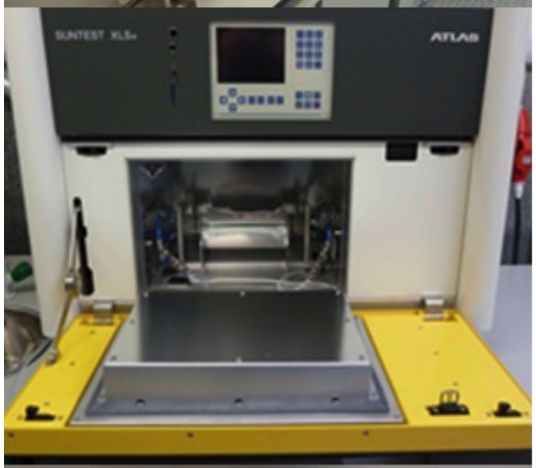
SSV = 4.0 g/L; T = 30ºC; Sludge Age = 21 days

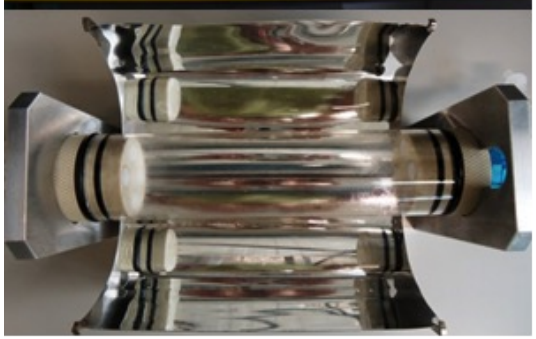
- Nitrification Cycle of 18 hours + Denitrification Cycle of 6 hours;
- Complete Removal of Ammonium ions;
- Almost Complete Removal of Nitrites;
- Methanol was Added as External Carbon Source for the Denitrification Reaction;
- Low Values of Alkalinity after the Biological Treatment;

Lab-Pilot-Pre-Industrial Scale Photoreactors

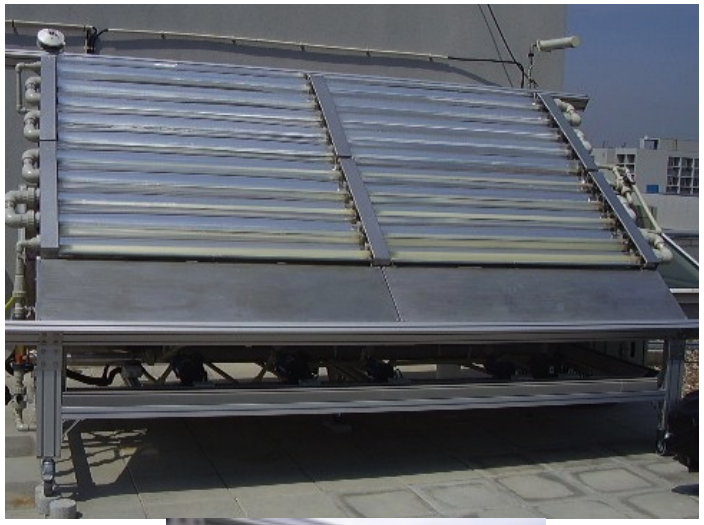
Lab-Scale



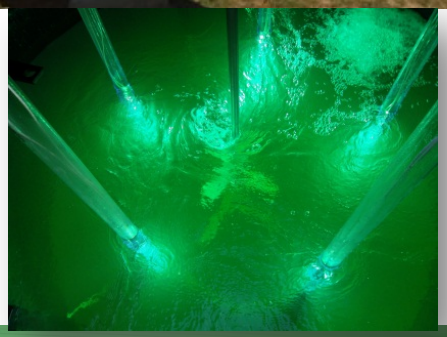




Pilot Scale



Pre-Industrial Plant

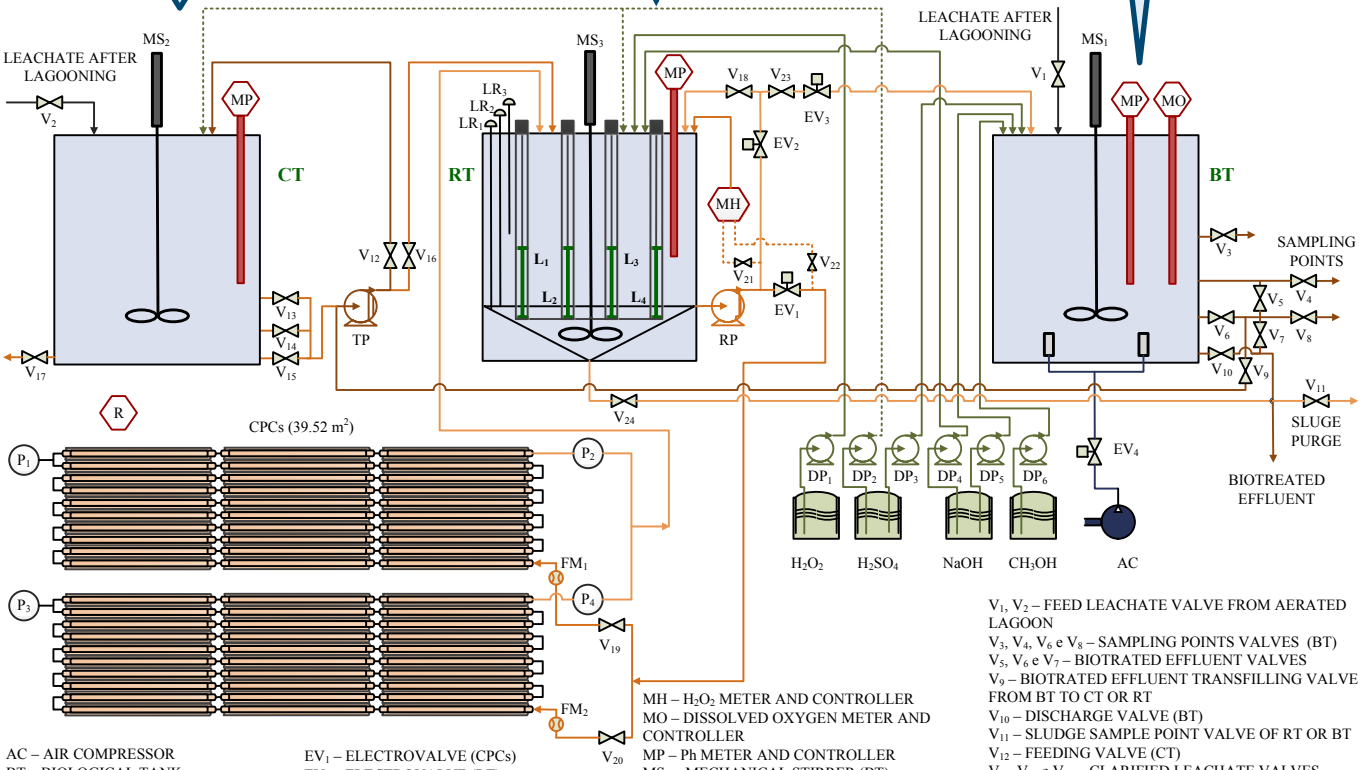


Multistage Treatment System For Leachates

Coagulation Tank (3.0 m³)

Recirculation Tank (2.5 m³)

Biological Tank (3.5 m³)



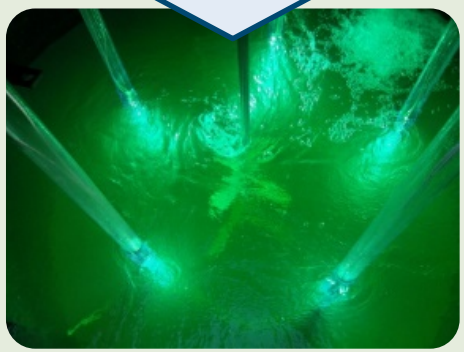
AC – AIR COMPRESSOR
BT – BIOLOGICAL TANK
CT – COAGULATION TANK
DP_1 – H_2O_2 DOSING PUMP
DP_2 – H_2SO_4 DOSING PUMP (CT)
DP_3 – H_2SO_4 DOSING PUMP (BT)
DP_4 – NaOH DOSING PUMP (RT)
DP_5 – NaOH DOSING PUMP (BT)
DP_6 – CH_3OH DOSING PUMP

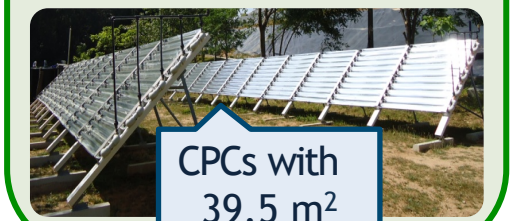
EV_1 – ELECTROVALVE (CPCs)
EV_2 – ELECTROVALVE (RT)
EV_3 – ELECTROVALVE (BT)
EV_4 – ELECTROVALVE (BT)
FM_1 e FM_2 – FLOWMETERS
L_1, L_2, L_3 e L_4 – UV-VIS LAMPS
LR_1 – REFERENCE FLUID LEVEL ROD
LR_2 – MINIMUM FLUID LEVEL ROD
LR_3 – MAXIMUM FLUID LEVEL ROD

MH – H_2O_2 METER AND CONTROLLER
MO – DISSOLVED OXYGEN METER AND CONTROLLER
MP – Ph METER AND CONTROLLER
MS_1 – MECHANICAL STIRRER (BT)
MS_2 – MECHANICAL STIRRER (CT)
MS_3 – MECHANICAL STIRRER (RT)
P_1, P_2, P_3 e P_4 – PURGE
R - RADIOMETER
RP – RECIRCULATION PUMP
RT – RECIRCULATION TANK
TP – TRANSFILLING PUMP

V_1, V_2 – FEED LEACHATE VALVE FROM AERATED LAGOON
V_3, V_4, V_6 e V_8 – SAMPLING POINTS VALVES (BT)
V_5, V_6 e V_7 – BIOTRATED EFFLUENT VALVES
V_9 – BIOTRATED EFFLUENT TRANSFILLING VALVE FROM BT TO CT OR RT
V_{10} – DISCHARGE VALVE (BT)
V_{11} – SLUDGE SAMPLE POINT VALVE OF RT OR BT
V_{12} – FEEDING VALVE (CT)
V_{13}, V_{14} e V_{15} – CLARIFIED LEACHATE VALVES
V_{16} – FEEDING VALVE (RT)
V_{17} – DISCHARGE VALVE (CT)
V_{18} – SECURITY VALVE (RT)
V_{19} e V_{20} – FEDDING VALVES (CPCs)
V_{21} e V_{22} – FEDDING VALVES (MH)
V_{23} – SECURITY VALVE (BT)
V_{24} – DISCHARGE VALVE (RT)

5x1250 W UV-Vis Lamps





CPCs with 39.5 m²

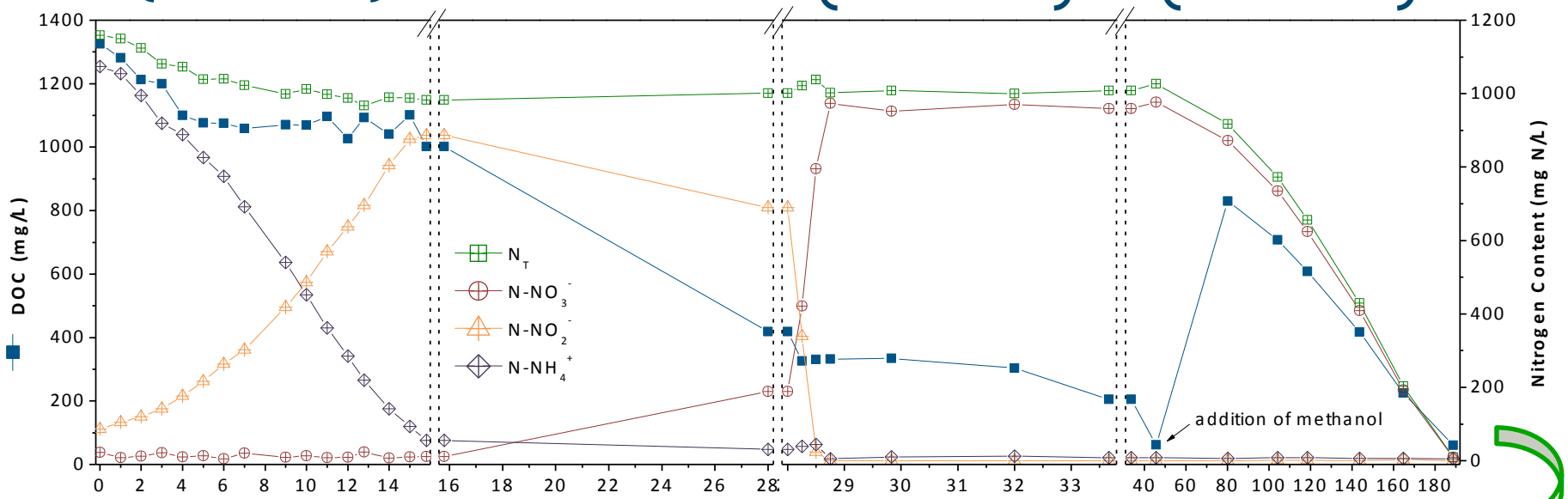
Multistage Treatment System For Leachates

1st Biological Oxidation
T = 25ºC
OD = 1 – 2 mg/L

Coagulation Sedimentation

Photo-Fenton Reaction
H_2O_2 = 127 mM
Q_{UV} = 10 kJ_{UV}/L

2nd Biological Oxidation
T = 27ºC
OD < 0.1 mg/L



Humic acids precipitation

Biodegradability enhancement

high treatment time due to the long biomass adaptation period

Denitrification:

- 3.4 mg NO_3^--N/(h.gVSS)
- Methanol consumption of 2.4 mg CH_3OH/mg NO_3^--N

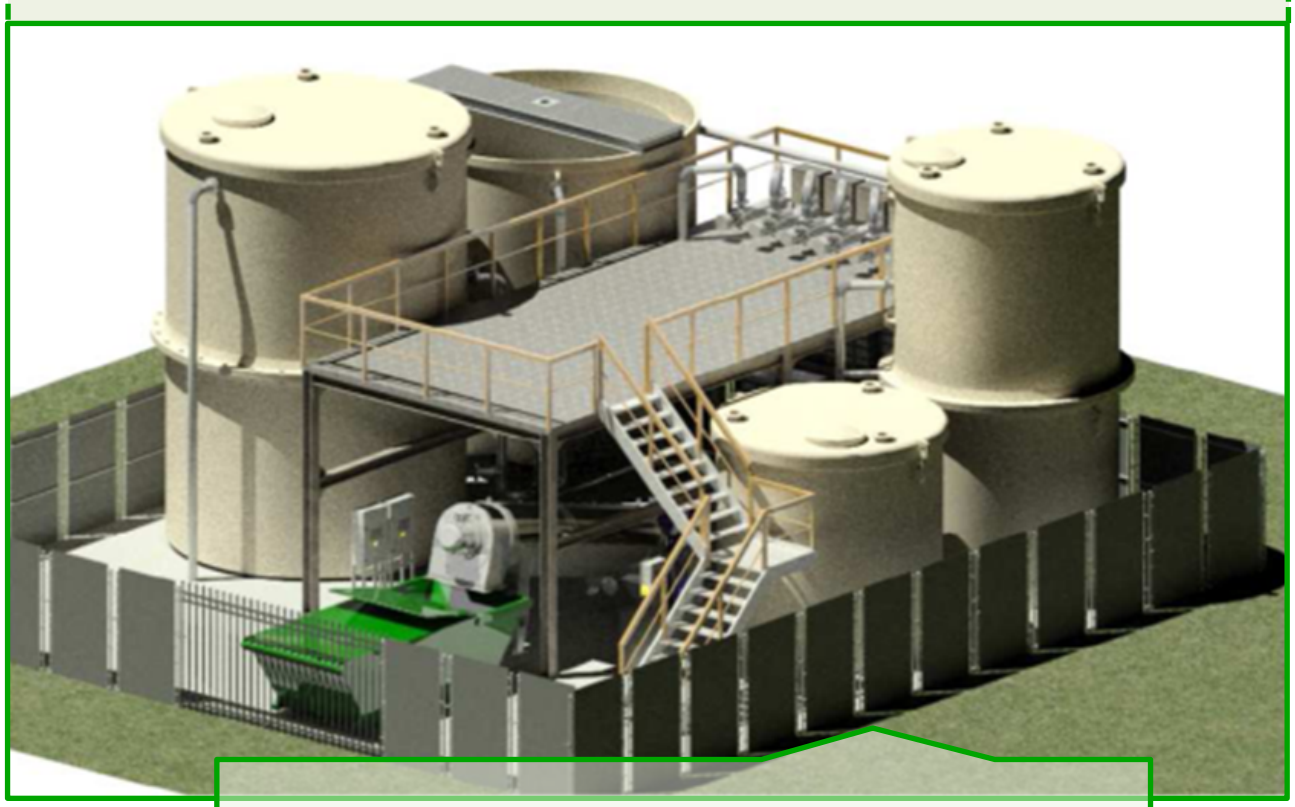
After all treatments, the wastewater presents the following characteristics:

- ⇨ COD = 105 mg O_2/L
- ⇨ BOD_5 = 13 mg O_2/L
- ⇨ Total Nitrogen = 14 mg N/L
- ⇨ SO_4^{2-} = 900 mg/L

which are in **agreement** with the discharge limits imposed by the **Portuguese Legislation** (Decree-law no 236/98)

Industrial Plant

Facility sized to treat 20 m^3/day of sanitary landfill leachate after aerated lagoon

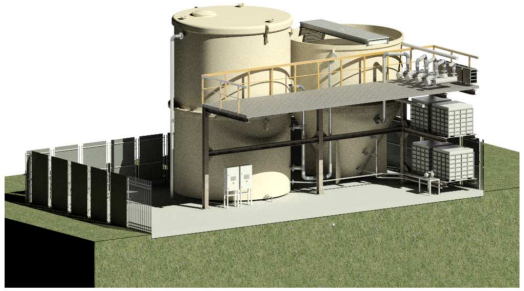


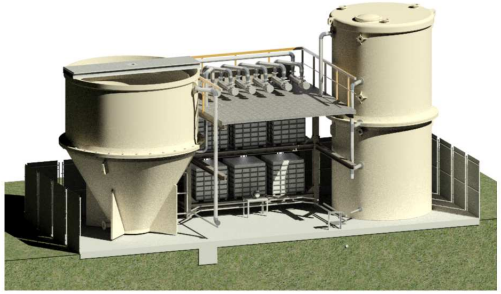
Project AdvancedLFT

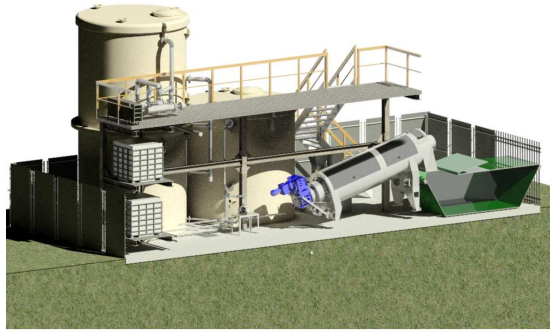
Partnership FEUP/EFACEC

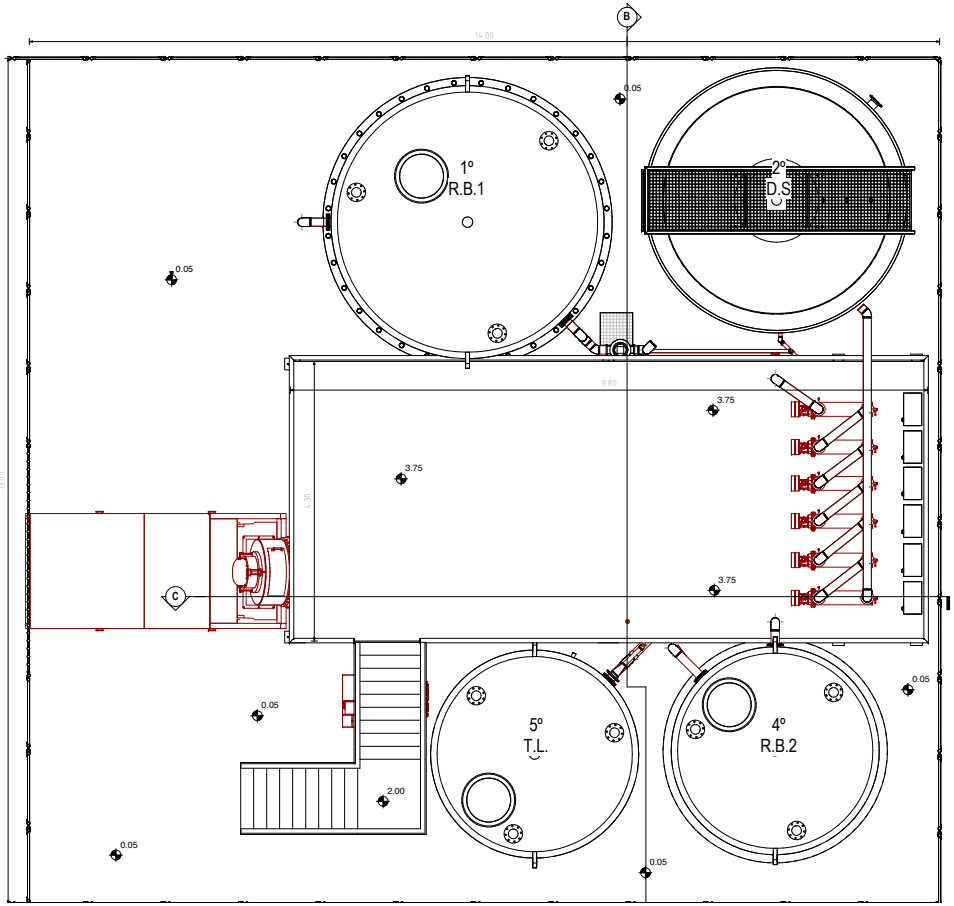
(funded by QREN)

Industrial Plant

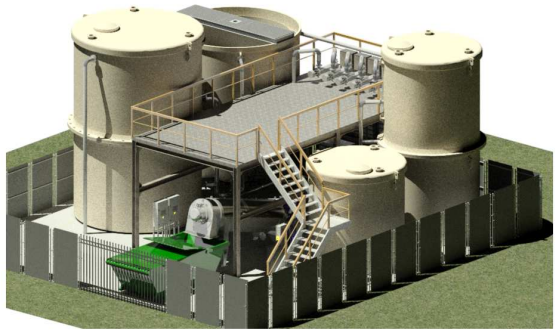








LEGENDA DOS ORGÃOS	
	Designação
1º R.B.1	Reactor Biológico 1
4º R.B.2	Reactor Biológico 2
5º T.L.	Tanque de Lamas



Rev.	Alteração	Desenhou	Data

PROJECTISTA

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ADVANCED LFT

CLIENTE

EQUIPAMENTO ELECTROMECÂNICO

IMPLANTAÇÃO GERAL (PLANTA DE COBERTURA)

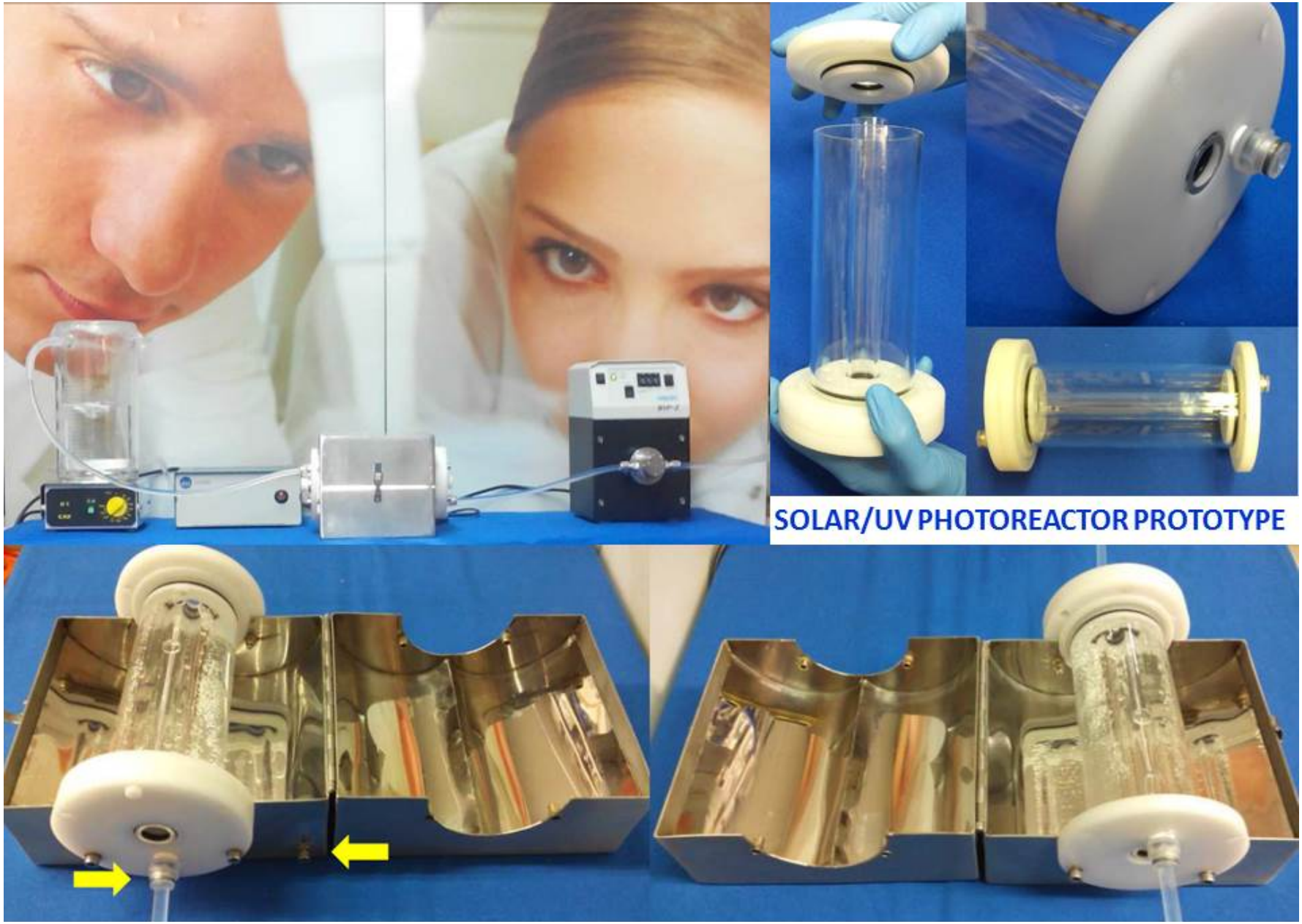
	NOME	RUBRICA	NÚMERO	REVISÃO

Industrial Plant

Industrial Plant

Industrial Plant

New Solar/UV Photoreactor Prototype



Conclusions

- Multistage Treatment System for the Treatment of Mature Leachates, achieving a Final Effluent with a COD Below 150 mg O_2/L and Total Nitrogen Below 15 mg N/L ;
- Biological Oxidation System: i) Biodegradable Organic Fraction Removal; ii) Nitrogen Content Removal Through Nitrification/Denitrification Reactions; iii) Alkalinity Removal;
- Coagulation/Sedimentation: i) TSS removal; ii) Humic Acids Removal; iii) Increase Leachate Transmissibility;
- Photo-Oxidation (Photo-Fenton): i) Degradation of the Recalcitrant Fraction of the Leachate (mainly Fulvic Acids); ii) Improve Leachate Biodegradability; iii) Oxidation of Nitrogen Organic Compounds to Ammonium, Nitrates or Nitrites;
- Biological Oxidation System: i) Biodegradable Organic Fraction Removal; ii) Nitrogen Content Removal Through Nitrification/Denitrification Reactions;
- Nitrification/Denitrification Reactions Rates Depends Significantly on the Leachate Temperature and pH.

Acknowledgements

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- LSRE (Laboratory of Separation and Reaction Engineering)
- Efacec Engenharia S.A.
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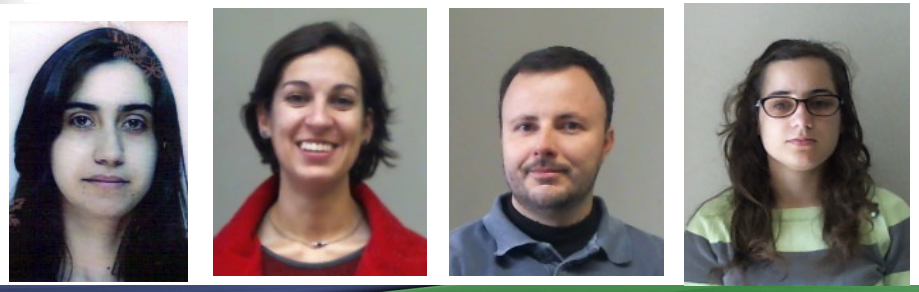
- FCT (Foundation For Science And Technology)
  - PhD and Postdoctoral Scholarships



EPOA/CIPOA

2015

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The conference topics will include:

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- Photo-Fenton;
- Photocatalysis;
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- AOPs/Membrane;
- Electrochemical Processes;
- Process Monitoring and Control;
- Solar-Driven Applications;
- Pilot Plant Scale Applications;
- AOP Applied to Contaminated Soil and Air;
- AOP Applied to Water Disinfection;
- AOP Applied to Wastewater Decontamination.

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