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Integration of Electrochemical Advanced Oxidation Processes in a Multistage System For Sanitary Landfill Leachate Remediation

AOPs PhD School

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

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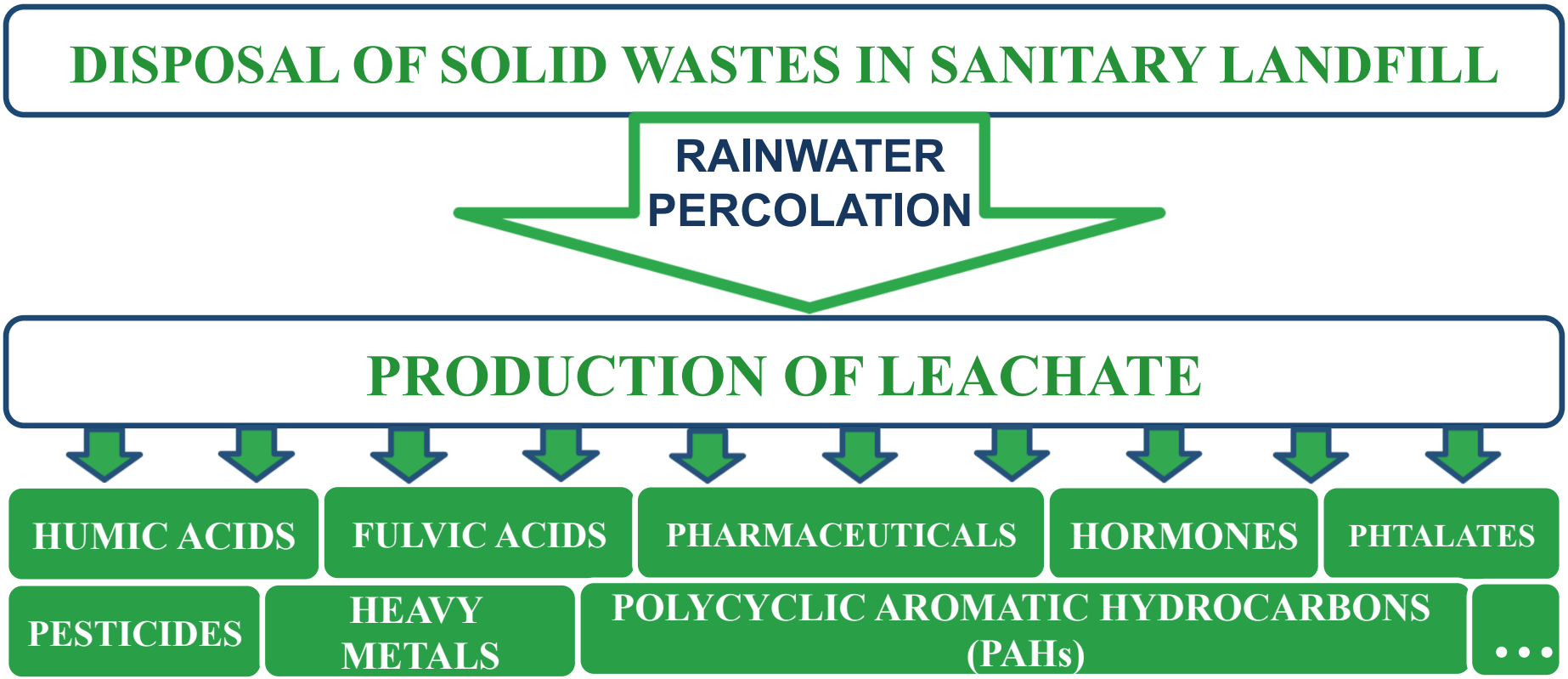
CONTENTS

INTRODUCTION

SANITARY LANDFILL LEACHATE



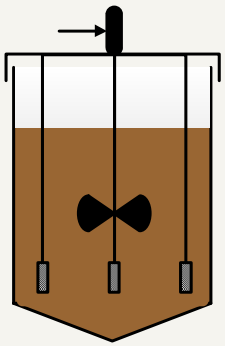
A. Baun, A. Ledin, L.A.,Reitzel, P.L. Bjerg, T.H. Christensen, Xenobiotic organic compounds in leachates from ten Danish MSW landfills-chemical analysis and toxicity tests. Water Research 38 (2004) 3845-3858.

INTRODUCTION

OBJECTIVE

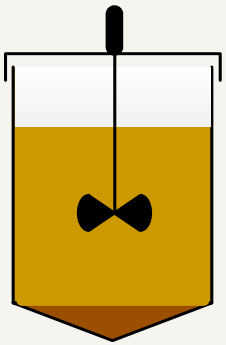
- To incorporate an EAOP stage in the following multistage strategy system for sanitary landfill leachate remediation:

1st BIOLOGICAL PROCESS



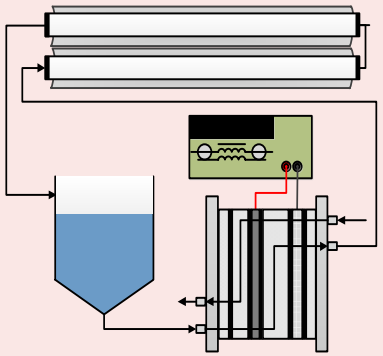
- BIODEGRADABLE ORGANIC FRACTION DEGRADATION
- NITRIFICATION
- ALKALINITY REMOVAL

COAGULATION



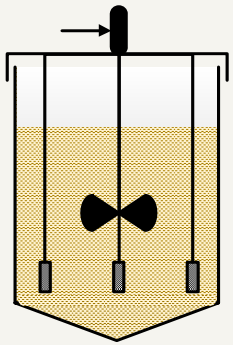
- HUMIC ACIDS REMOVAL
- SUSPENDED SOLIDS REMOVAL

EAOP



- RECALCITRANT ORGANIC FRACTION DEGRADATION
- BIODEGRADABILITY ENHANCEMENT

2nd BIOLOGICAL PROCESS



- EAOP BIODEGRADABLE ORGANIC FRACTION DEGRADATION
- DENITRIFICATION

INTRODUCTION

ELECTROCHEMICAL ADVANCED OXIDATION PROCESSES (EAOP)

PEF – PHOTOELECTRO-FENTON **SPEF – SOLAR PHOTOELECTRO-FENTON**

EF – ELECTRO-FENTON

AO-H_2O_2 – ANODIC OXIDATION WITH ELECTROGENERATED H_2O_2

WATER OXIDATION ON THE ANODE SURFACE: $M + H_2O \rightarrow M(^{\bullet}OH) + H^+ + e^-$

H_2O_2 ELECTROGENERATION AT THE CATHODE: $O_{2(g)} + 2\,H^+ + 2\,e^- \rightarrow H_2O_2$

FENTON'S REACTION: $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^-$

Fe^{2+} REGENERATION AT THE CATHODE: $Fe^{3+} + e^- \rightarrow Fe^{2+}$

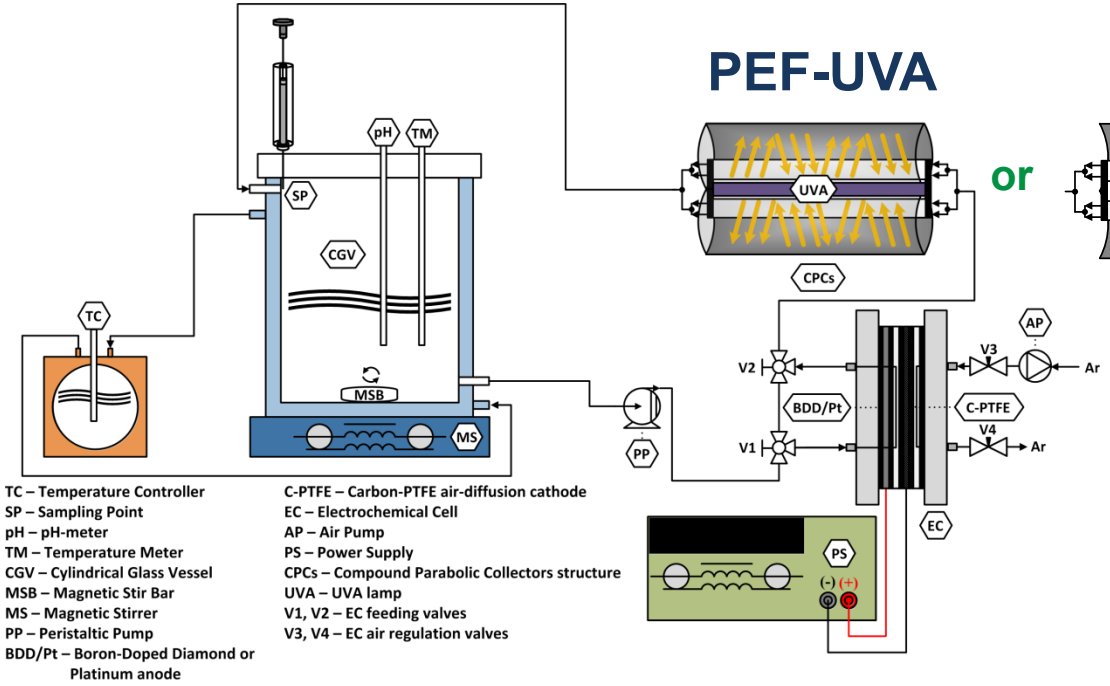
PHOTOLYSIS OF $FeOH^{2+}$: $FeOH^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH$

PHOTOLYSIS OF Fe(III)-ORGANICS COMPLEXES: $Fe^{3+}(L)_n + h\nu \rightarrow Fe^{2+}(L)_{n-1} + L_{ox}^{\bullet}$

E. Brillas, I. Sirés, M.A. Oturan, Electro-Fenton process and related electrochemical technologies based on Fenton's reaction chemistry. Chemical Reviews 109 (2009) 6570-6631.

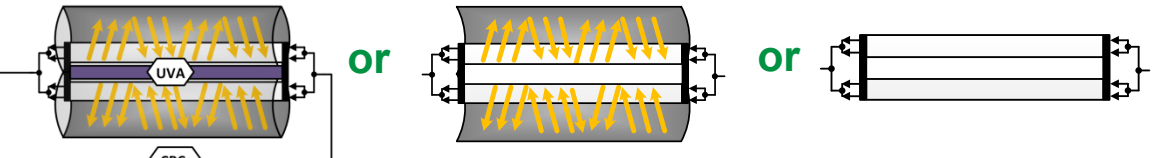
EXPERIMENTAL

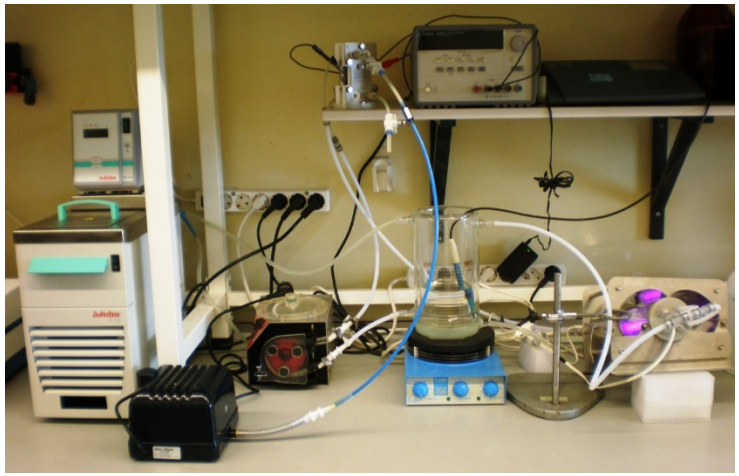
EAOPs SYSTEM AT LAB-SCALE



TC – Temperature Controller
SP – Sampling Point
pH – pH-meter
TM – Temperature Meter
CGV – Cylindrical Glass Vessel
MSB – Magnetic Stir Bar
MS – Magnetic Stirrer
PP – Peristaltic Pump
BDD/Pt – Boron-Doped Diamond or Platinum anode
C-PTFE – Carbon-PTFE air-diffusion cathode
EC – Electrochemical Cell
AP – Air Pump
PS – Power Supply
CPCs – Compound Parabolic Collectors structure
UVA – UVA lamp
V1, V2 – EC feeding valves
V3, V4 – EC air regulation valves

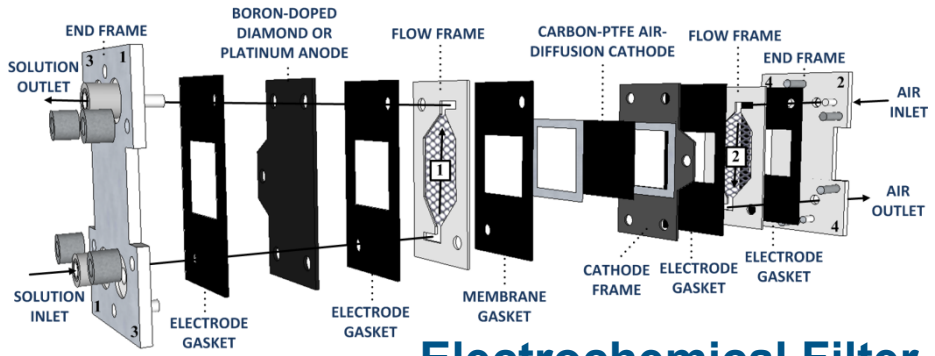
PEF-UVA or **SPEF** or **AO-H_2O_2 and EF**

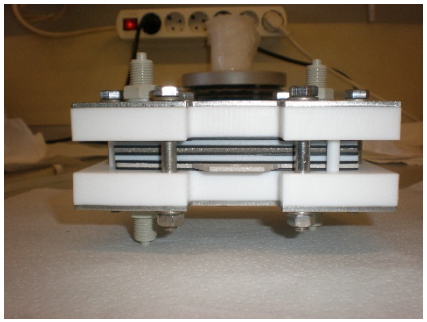




BDD/CARBON–PTFE AIR-DIFFUSION

10 cm^2 active area

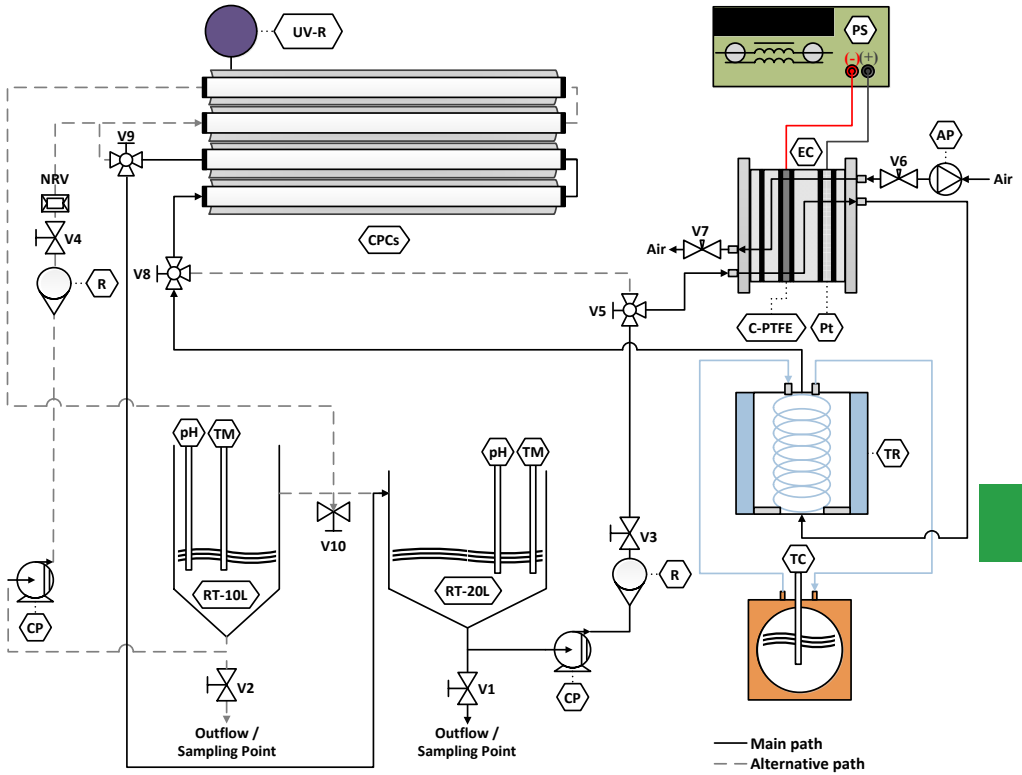




Electrochemical Filter-Press MicroFlowCell

EXPERIMENTAL

EAOPs SYSTEM AT PILOT-SCALE

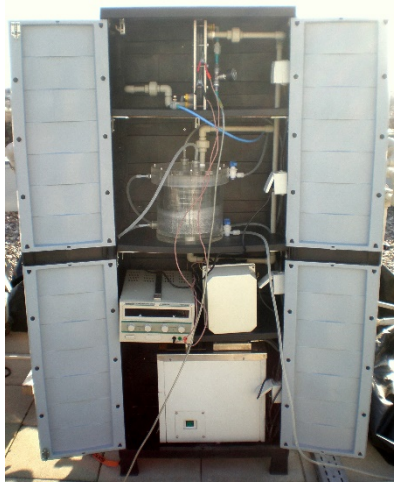


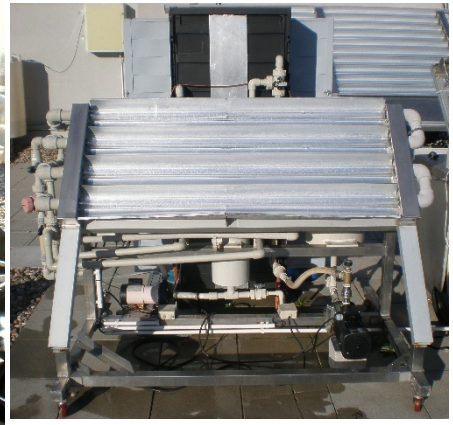
Main path
Alternative path

pH – pH-meter
TM – Temperature Meter
RT-20L – Recirculation Tank with 20 L capacity
RT-10L – Recirculation Tank with 10 L capacity
CP – Centrifugal Pump
R – Rotameter
PS – Power Supply
EC – Electrochemical Cell

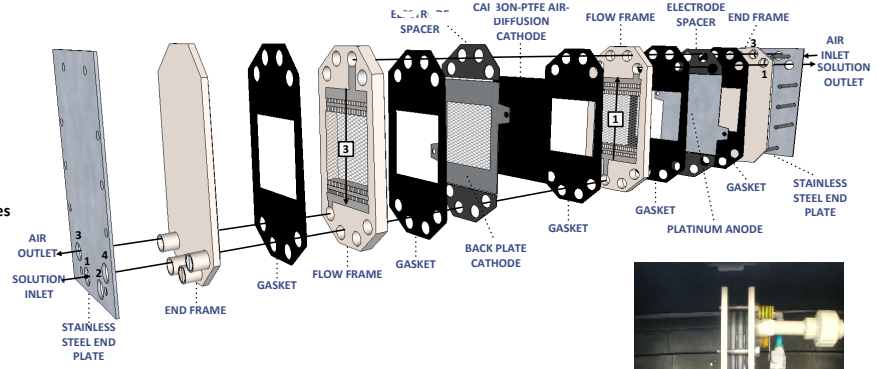
AP – Air Pump
C-PTFE – Carbon-PTFE air-diffusion cathode
Pt – Platinum anode
TR – Thermostated Reactor
TC – Temperature Controller
CPCs – Compound Parabolic Collectors
UV-R – UV Radiometer

V1, V2 – Recirculation / Discharge valves
V3, V4 – Flow rate control valves
V5 – EC feeding valve
V6, V7 – EC air regulation valves
V8, V9 – CPCs configuration valves
V10 – RTs feeding valve
NRV – Non-Return Valve





Pt/CARBON–PTFE AIR-DIFFUSION



100 cm² active area

RESULTS AND DISCUSSION

RAW, BIO-TREATED AND COAGULATED LANDFILL LEACHATE

PARAMETER (UNIT)	RAW	AFTER 1st BIOLOGICAL TREATMENT	AFTER COAGULATION
pH	8.2-9.0	7.0-8.0	2.2-2.9
DIC (mg L^{-1})	1950-2664	11-20	0.0-2.6
DOC (mg L^{-1})	1222-1460	956-1062	337-430
COD (mg O_2 L^{-1})	3106-4057	2870-3201	1030-1505
BOD_5 (mg O_2 L^{-1})	180-300	16-18	1-10
TSS (mg L^{-1})	525-630	441-580	140-230
N-NH_4^+ (mg L^{-1})	1300-1355	<0.04-20	<0.04-9
N-NO_2^- (mg L^{-1})	49-84	5-25	3-18
N-NO_3^- (mg L^{-1})	2-17	1020-1078	1035-1192
SO_4^{2-} (mg L^{-1})	46-120	44-83	1749-1917
Cl^- (mg L^{-1})	2220-2780	2211-2906	3046-3822

1st BIOLOGICAL TREATMENT

- CONSUMPTION OF INORGANIC CARBON AND ALKALINITY
- 13-33% OF DOC REMOVAL AND 90-95% OF BOD_5 REMOVAL
- CONVERSION OF NH_4^+ TO NO_3^-

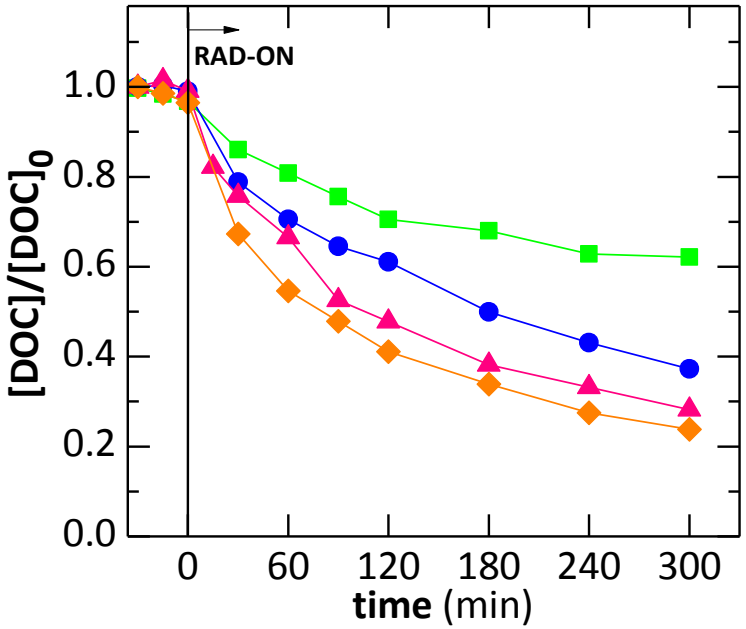
COAGULATION

- LARGE DECOLORIZATION DUE TO HUMIC ACIDS PRECIPITATION
- TSS REMOVAL OF 47-57%
- 63-65% OF DOC REMOVAL

RESULTS AND DISCUSSION - EAOPs

INFLUENCE OF CURRENT DENSITY

Parasitic Reactions: Anodic Oxidation of BDD(•OH) to O_2



(■) 25 mA cm^{-2}
(●) 100 mA cm^{-2}
(▲) 200 mA cm^{-2}
(◆) 300 mA cm^{-2}
PEF-UVA
Lab-scale
BDD anode
20 ºC
pH = 2.8
60 mg Fe^{2+} L^{-1}

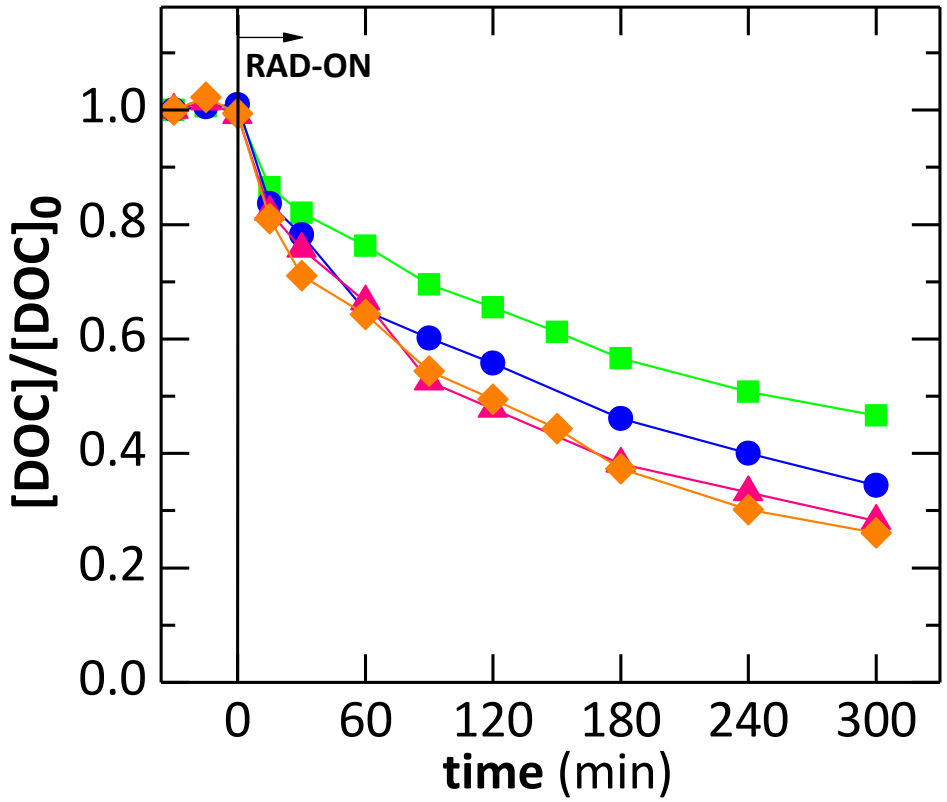
BEST CURRENT DENSITY: 200 mA cm^{-2}

	25 mA cm^{-2}	100 mA cm^{-2}	200 mA cm^{-2}	300 mA cm^{-2}
FINAL DOC REMOVAL (%)	38	63	72	76
ENERGY CONSUMPTION (kWh m^{-3})	4.8	54	95	176
FINAL [H_2O_2] (mg L^{-1})	51	312	769	880

- SIMILAR EFFICIENCY ON DOC REMOVAL FOR CURRENT DENSITIES ABOVE 200 mA cm^{-2}
- H_2O_2 ALWAYS ACCUMULATED IN EXCESS FOR ALL APPLIED CURRENT DENSITIES

RESULTS AND DISCUSSION - EAOPs

INFLUENCE OF INITIAL TOTAL DISSOLVED IRON



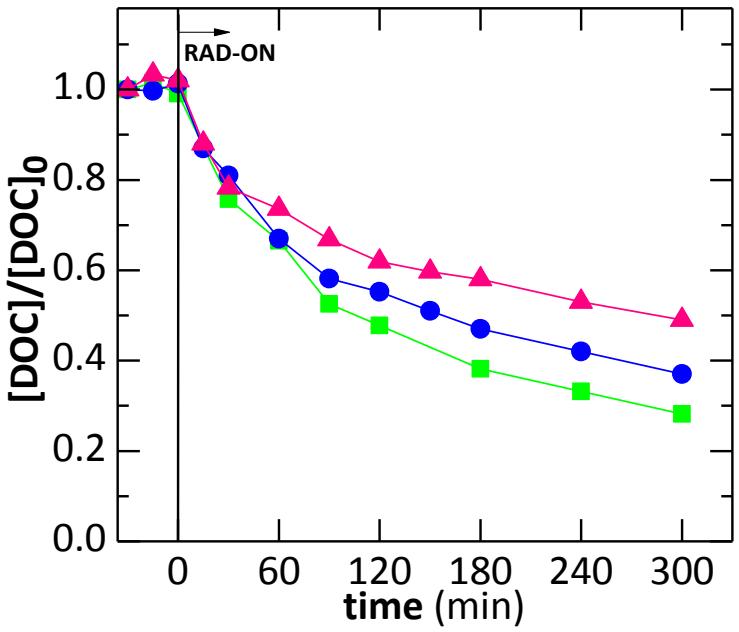
(■) 20 mg Fe^{2+} L^{-1}
(●) 40 mg Fe^{2+} L^{-1}
(▲) 60 mg Fe^{2+} L^{-1}
(◆) 80 mg Fe^{2+} L^{-1}
PEF-UVA
Lab-scale
BDD anode
200 mA cm^{-2}
20 ºC
pH = 2.8

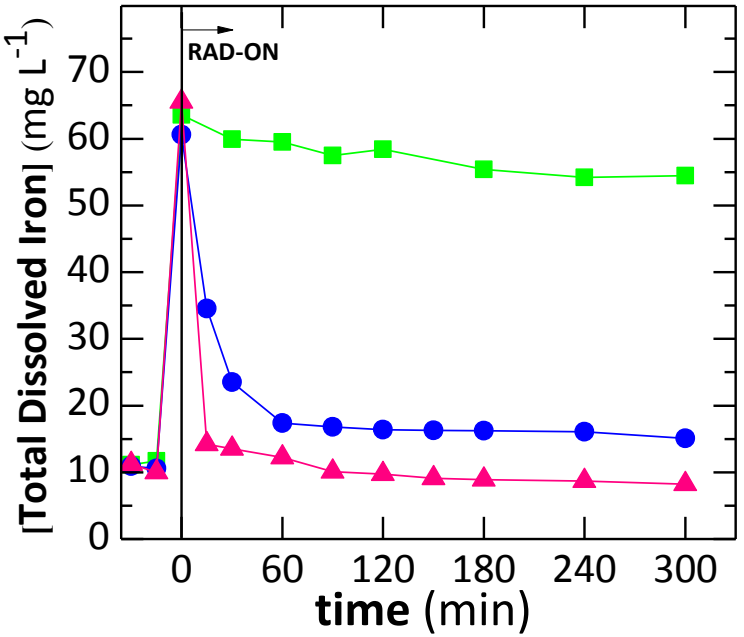
BEST INITIAL DISSOLVED IRON CONCENTRATION: 60 mg Fe^{2+} L^{-1}

SIMILAR EFFICIENCY ON DOC REMOVAL FOR INITIAL TOTAL DISSOLVED IRON CONCENTRATIONS ABOVE 60 mg Fe^{2+} L^{-1}

RESULTS AND DISCUSSION - EAOPs

INFLUENCE OF pH





(■) pH = 2.8
(●) pH = 3.5
(▲) pH = 4.0
PEF-UVA
Lab-scale
BDD anode
200 mA cm^{-2}
60 mg Fe^{2+} L^{-1}
20 ºC

BEST pH: 2.8

FASTEST MINERALIZATION AT pH = 2.8
TOGETHER WITH ALMOST NULL IRON PRECIPITATION

RESULTS AND DISCUSSION - EAOPs

INFLUENCE OF TEMPERATURE

PEF-UVA

BDD anode; 200 mA cm^{-2}

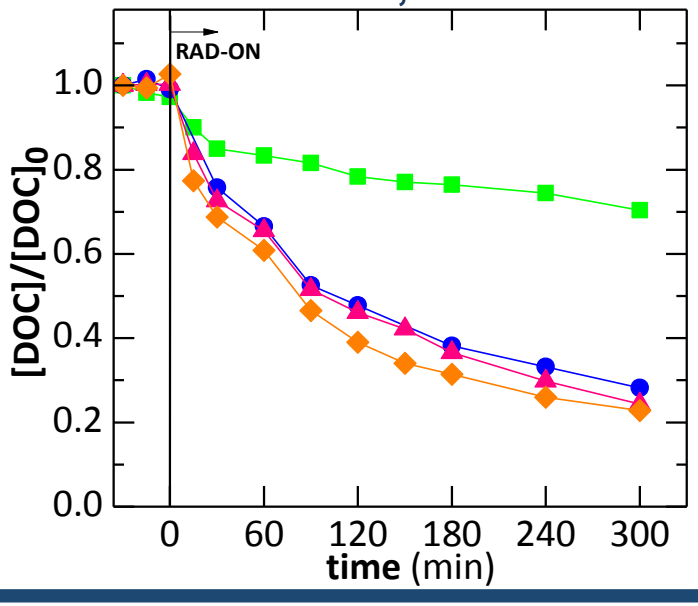
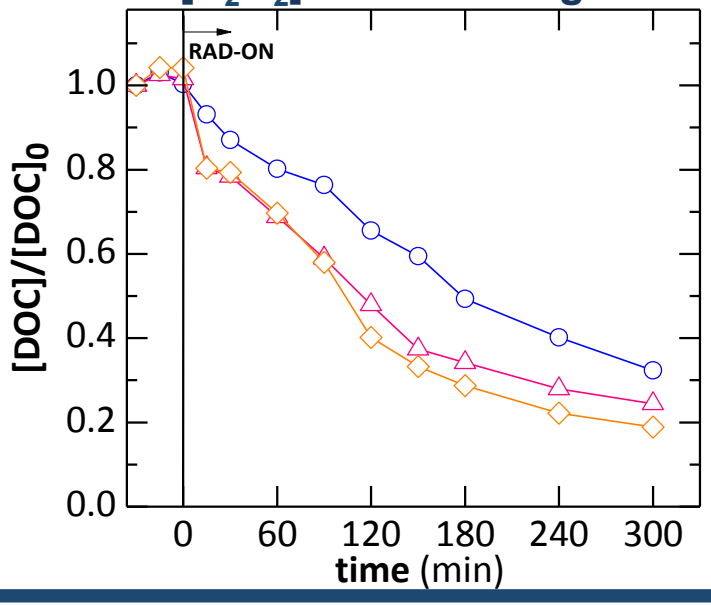


PHOTO-FENTON-UVA

$[H_2O_2]$ = 200-400 mg L^{-1}



(■) 15 °C
(●) 20 °C
(▲) 30 °C
(◆) 40 °C
Lab-scale
60 mg Fe^{2+} L^{-1}
pH = 2.8

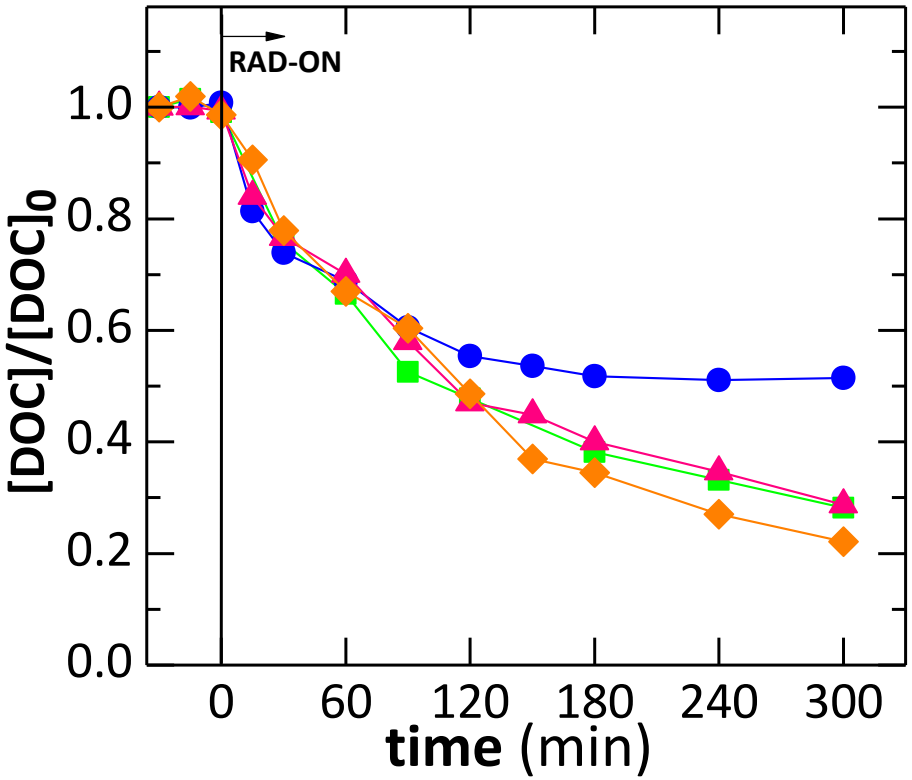
PEF-UVA: SIMILAR MINERALIZATION FOR TEMPERATURES FROM 20 TO 40 °C, ALTHOUGH TEMPERATURES ABOVE 20 °C LED TO IRON PRECIPITATION

PHOTO-FENTON-UVA: FASTER MINERALIZATION AT 30 AND 40 °C THAN AT 20 °C

LARGER PARTICIPATION OF ELECTROCHEMICAL REACTIONS ON THE EFFLUENT MINERALIZATION AT 20 °C THAN AT 30 AND 40 °C

RESULTS AND DISCUSSION - EAOPs

INFLUENCE OF RADIATION SOURCE



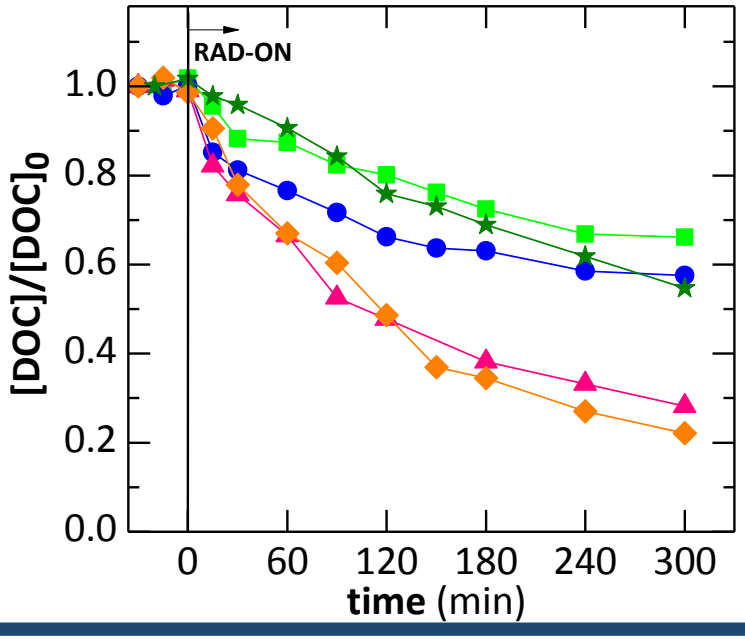
(■) UVA LAMP
(●) UVA-Vis LAMP
(▲) UVC LAMP
(◆) NATURAL SUNLIGHT
PEF/SPEF
Lab-scale
BDD anode
200 mA cm^{-2}
20 ºC
pH = 2.8

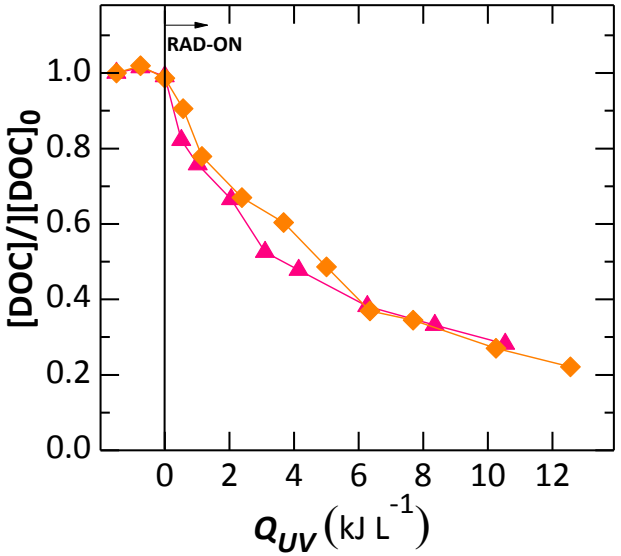
SIMILAR MINERALIZATION USING UVA AND UVC LAMPS AND NATURAL SUNLIGHT

LOWER MINERALIZATION USING UVA-Vis LAMP MAINLY FOR LONGER REACTION TIMES

RESULTS AND DISCUSSION - EAOPs

COMPARATIVE APPLICATION OF EAOPs





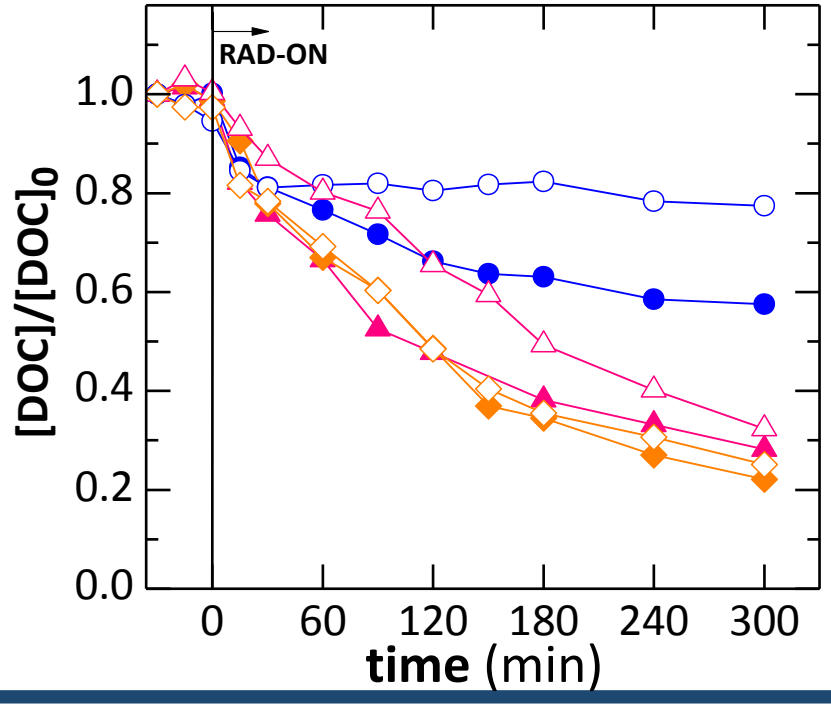
(★) AO
(■) AO-H_2O_2
(●) EF
(▲) PEF-UVA
(◆) SPEF
Lab-scale
BDD anode
200 mA cm^{-2}
60 mg Fe^{2+} L^{-1}
20 ºC
pH = 2.8

EFFICIENCY OF EAOPs: AO-H_2O_2 < AO < EF < PEF-UVA ≈ SPEF

- LARGE PARTICIPATION OF BDD(•OH) ON THE EFFLUENT MINERALIZATION
- AO vs AO-H_2O_2: LOSS OF •OH VIA H_2O_2 + •OH → H_2O + HO_2• IN AO-H_2O_2 AND/OR FORMATION OF MORE RECALCITRANT BY-PRODUCTS IN AO-H_2O_2
- SLIGHTLY MINERALIZATION IMPROVEMENT FROM •OH PRODUCED BY FENTON´S REACTION
- CRUCIAL ROLE OF RADIATION PROVIDED IN PEF AND SPEF ON THE EFFLUENT MINERALIZATION BECAUSE OF THE ADDITIONAL •OH PRODUCTION AND Fe^{2+} REGENERATION FROM PHOTOREDUCTION OF Fe(III) COMPLEXES

RESULTS AND DISCUSSION - EAOPs

EAOPs *vs* AOPs



(●) EF
(○) FENTON
(▲) PEF-UVA
(△) PHOTO-FENTON-UVA
(◆) SPEF
(◇) SOLAR PHOTO-FENTON
Lab-scale
BDD anode (in EAOPs)
200 mA cm^{-2} (in EAOPs)
$[H_2O_2]$ = 200-400 mg L^{-1} (in AOPs)
60 mg Fe^{2+} L^{-1}
20 ºC
pH = 2.8

HIGH SUPERIORITY OF EF OVER FENTON

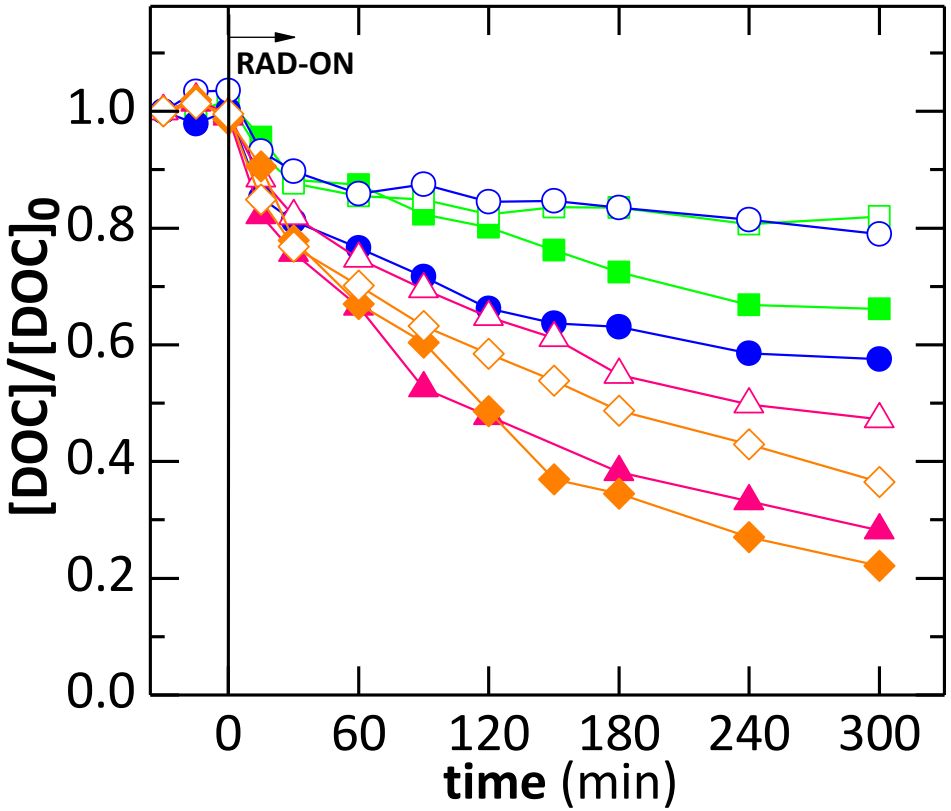
HIGH SUPERIORITY OF PEF-UVA OVER PHOTO-FENTON-UVA

SIMILARITY BETWEEN SPEF AND SOLAR PHOTO-FENTON

MORE IMPORTANT ROLE OF OXIDANTS PRODUCED BY PHOTOREDUCTION OF Fe(III) COMPLEXES COMPARATIVELY TO THE ELECTROCHEMICAL GENERATED OXIDANTS

RESULTS AND DISCUSSION - EAOPs

INFLUENCE OF ANODE MATERIAL



(■) AO-H_2O_2-BDD
(□) AO-H_2O_2-Pt
(●) EF-BDD
(○) EF-Pt
(▲) PEF-UVA-BDD
(△) PEF-UVA-Pt
(◆) SPEF-BDD
(◇) SPEF-Pt
PEF-UVA
Lab-scale
200 mA cm^{-2}
60 mg Fe^{2+} L^{-1}
20 ºC
pH = 2.8

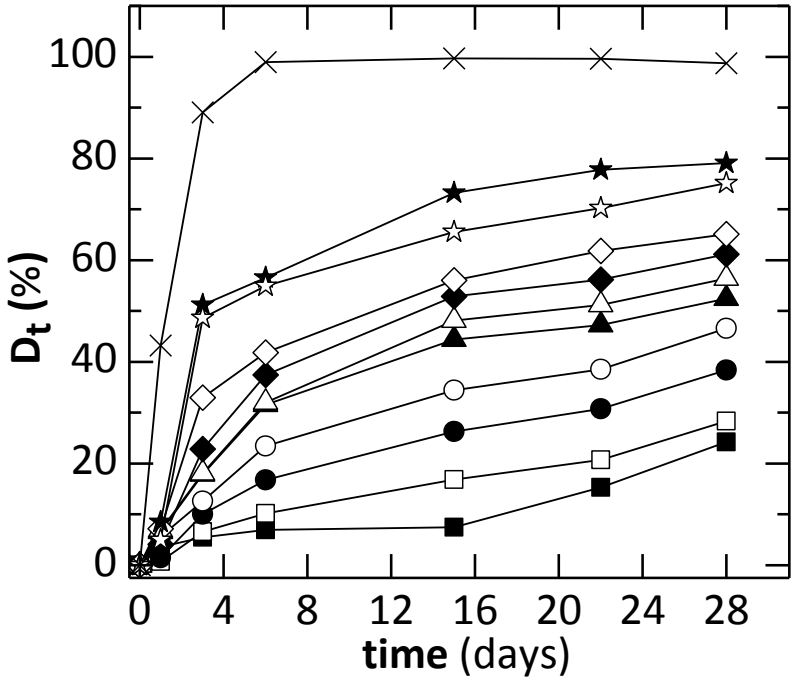
BEST ANODE MATERIAL: BDD

FASTER MINERALIZATION FOR ALL EAOPs WITH BDD ANODE THAN WITH Pt ANODE

IMPORTANT ROLE OF BDD(•OH) ON THE ORGANICS DEGRADATION EVEN UNDER SOLAR LIGHT

RESULTS AND DISCUSSION - EAOPs

BIODEGRADABILITY ENHANCEMENT – ZAHN-WELLENS TEST



SPEF

Pilot-scale

Pt anode

200 mA cm^{-2} (in EAOPs)

60 mg Fe^{2+} L^{-1}

20 ºC

pH = 2.8

BEST DOC TO STOP SPEF:
163 mg L^{-1}

ELECTRICAL CONSUMPTION:
36 kWh m^{-3}

	S_0	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9
DOC (day 0) (mg L^{-1})	347	314	267	250	211	186	163	140	110	85
DOC (day 28) (mg L^{-1})	266	232	168	138	105	86	69	55	30	28
COD (day 0) (mg O_2 L^{-1})	950	925	720	690	445	370	290	268	206	160
COD (day 28) (mg O_2 L^{-1})	904	602	442	332	228	158	102	85	50	47
BOD_5 (day 0) (mg O_2 L^{-1})	24	24	32	44	64	64	68	72	72	55
D_t (day 28) (%)	24	27	38	47	52	56	61	65	79	75

LEGISLATION LIMITS:
125 (EU)
150 (PT)

CONCLUSIONS

- The remediation of a raw sanitary landfill leachate by the application a multistage treatment strategy composed of biological treatment/ coagulation/EAOP/biological treatment was successful concerning the elimination of organic matter and nitrogen compounds.
- Best PEF operational conditions: 200 mA cm^{-2}, 60 mg Fe^{2+} L^{-1}, pH of 2.8, 20-40 ^{o}C, UVA, UVC or natural sunlight and BDD anode.
- High superiority of EF over Fenton, high superiority of PEF-UVA over photo-Fenton-UVA and similarity between SPEF and solar photo-Fenton in terms of oxidation ability.
- Need of performing the electrochemical treatment up to reach ≈ 163 mg DOC L^{-1} to couple a further biological process.

ACKNOWLEDGEMENTS

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Laboratório de catálise e materiais
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PROGRAMA OPERACIONAL FACTORES DE COMPETITIVIDADE

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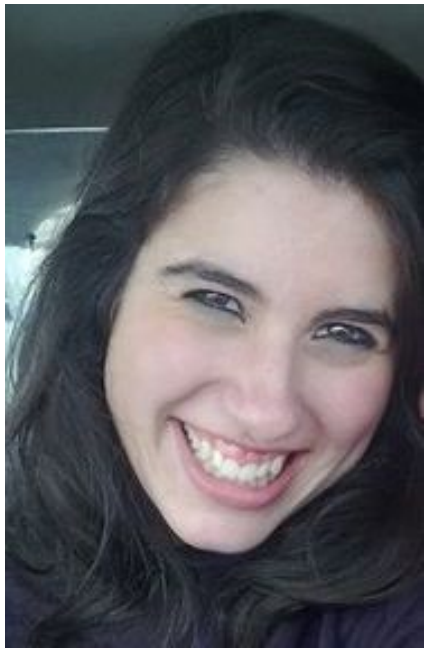

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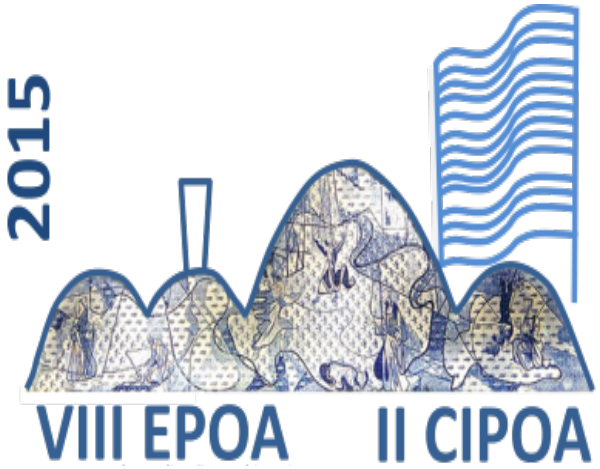

The conference topics will include:

- Fenton;
- Photo-Fenton;
- Photocatalysis;
- Ozonation;
- AOPs/Biological Oxidation;
- 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.

8° Encontro sobre Aplicações Ambientais de Processos Oxidativos Avançados (VII EPOA)

2° Congresso Ibero-americano de Processos Oxidativos Avançados (II CIPOA)

http://www.epoa8.desa.ufmg.br/

3 a 6 de Novembro de 2015 - Belo Horizonte – MG - Brasil

8ºEPOA
CHAIRWOMAN of EPOA- Prof. Camila Amorim

2ºCIPOA
CHAIRMAN of CIPOA – Doutor Vítor Vilar