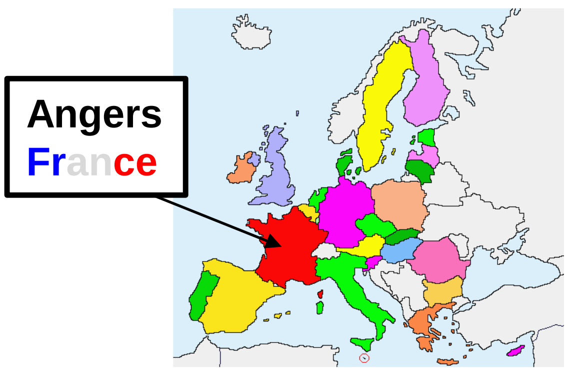
LE STUDIUM CONFERENCE
ORLÉANS | 2018

26-28 November 2018
Water micropollutants: from detection to removal

Carbon modified sensors dedicated to organic micropollutants analysis and innovant waters treatment (WT) aid



http://geihp.univ-angers.fr

M. PONTIÉ, professor
Angers University

KEYNOTE SPEAKER, **27th Novembre 9h45**

maxime.pontie@univ-angers.fr

Orléans, 27th November 2018

M. PONTIÉ, Professor at the University of Angers, FRANCE
Laboratory GEIHP EA3142, CHU Angers

maxime.pontie@univ-angers.fr

General outlines

1/ GENERAL INTRODUCTION

2/ COMMERCIALIZED ELECTROCHEMICAL SENSORS

3/ THE PROBLEM OF ORGANIC MICROPOLLUTANTS IN WATER RESSOURCES

4/ CASE STUDIES 1 : Electrochemical sensors development
⇒ UME, CPE, GCE, PGE DEVELOPMENTS DEDICATED TO ORGANIC MICROPOLLUTANTS

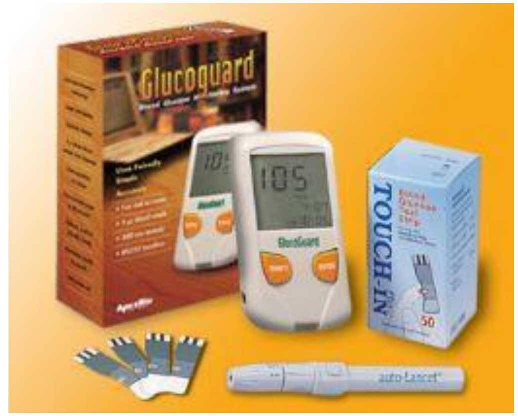
5/ CASE STUDIES 2 : Electrochemical analysis and WWT processes
⇒ BIOREACTORS DEVELOPMENT + NANOFILTRATION
⇒ ANTIBIOFILMS STRATEGIES ON UME &CPE

1/ GENERAL INTRODUCTION

need to measure, detect, monitor

MEDICAL / HEALTH

Self-diagnosis (glucose, lactate)



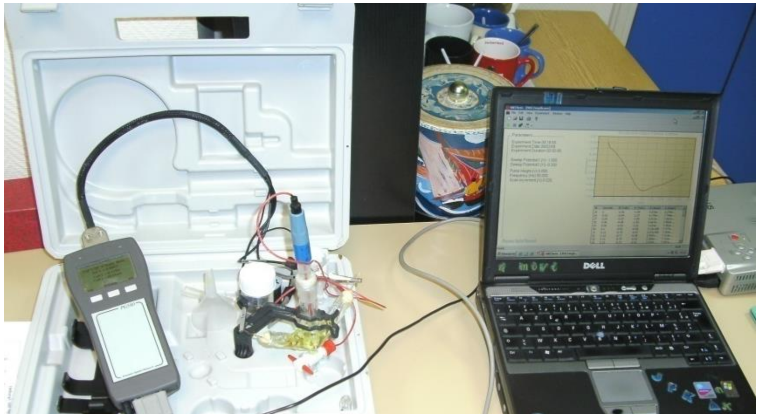
Multi-analysis
for emergencies

Multi-analysis for biological laboratories

for the patient
in his hospital room

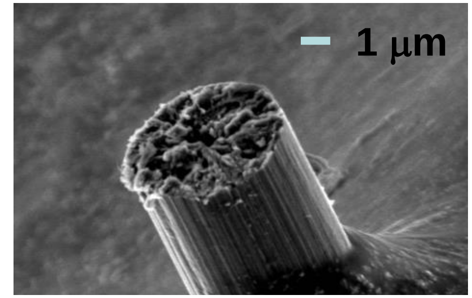
Studies interactions
drug receptor

ENVIRONMENTAL ANALYSIS



1st pesticide measurement kit (Nanosenso™, Angers Univ. 2010)

OUTSIDE THE LAB



UME

Nanosenso™, 2010, GA&P/GEPEA

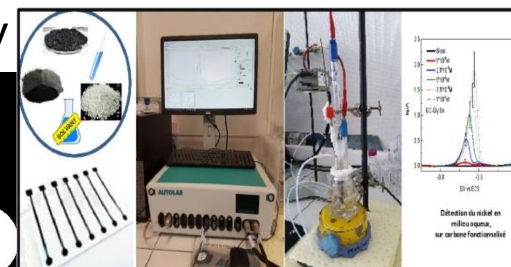
INSIDE THE LAB

Bacterial biosensor, BOD measurement

(Biosensors) GEPEA 2008 (Nantes)

Orléans University

PIVOTS



SPE

DSA TECHNOLOGIES • SMART MEDIA

Analysis for what ?

DIAGNOSIS

not only…

WATERS TREATMENT PROCESSES AID FOR THEIR INTENSIFICATION

2/ ELECTROCHEMICAL SENSORS

POTENTIOMETRIC, AMPEROMETRIC

Commercialized Sensors (1)

Kind of electrode	Species
Solid Membrane ❖ glass ❖ monocrystal ❖ compacted solids (powder)	H^+, Na^+, K^+, (Li^+, Rb^+, Ag^+) F^- Ag^+, Cd^{2+}, Cu^{2+}, Pb^{2+}, S^{2-}, Cl^-, Br^-, I^-, CN^-, SCN^-
Liquid membrane ❖ neutral transport ❖ ionics exchange	K^+, NH_4^+, Na^+, (Li^+, Ca^{2+}) Ca^{2+}, Cu^{2+}, Cl^-, BF_4^-, Mg^{2+}, NO_3^-, ClO_4^-, Organics anions and cations
Gaz sensors	NH_3, CO_2, SO_2, HCN, H_2S

Limit of detection (LOD) : 10^{-6} mol/L

Commercialized amperometric Sensors (2)

Kind of sensors	Companies
Solid membrane ❖ NO (oxydation in NO^+) ❖ O_2 (reduction in H_2O) ❖ inorganics micropollutants (reduction of Pb^{2+}; Cd^{2+}; Hg^{2+})	WPI (US) HACH LANGE (US) Some commercialized devices • Autolab (http://www.ecochemie.nl) • Palmsens (http://www.palmsens.com) • Origalys (http://www.origalys.com/fr/) • Metrohm (http://www.metrohm.com)
❖ **Organics micropollutants ➔**	**no devices commercialized**
Gaz detectors	O_2, H_2S

Limit of detection : 10^{-12} mol/L

3/ THE PROBLEM OF ORGANIC MICROPOLLUTANTS IN WATER RESSOURCES

All chemical substances detected in the form of traces and which are of human origin. There are 3 categories of micropollutants: organic, inorganic and organometallic [1].

Most of those compounds comes from industrial syntheses. These are products with a wide variety of uses : pesticides, biocides, cleaning agents ...

Emerging micropollutants are the drug molecules and their metabolites.

A PUBLIC AND ANALYTICAL HEALTH ISSUE

They are scattered in all compartments of the environment

They are found in trace amounts (submicromolar concentrations)

A NEED

Monitoring aquatic environments, our food and our body

A NECESSITY

Analysis and treatment of contaminated compartments

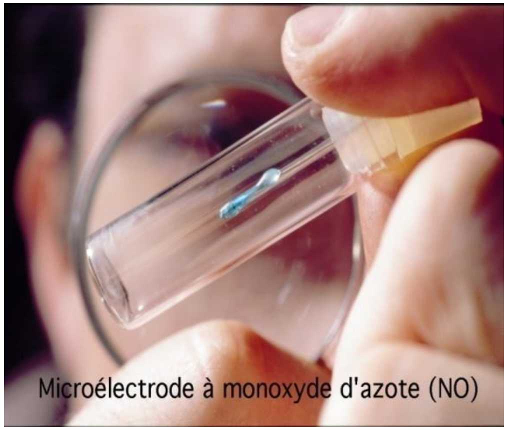
[1] **Chèvre N., Erkman S.,** Alerte aux micropolluants, Pesticides, biocides, détergents, médicaments et autres substances chimiques dans l'environnement, Nature et Environnement, **Collection Le Savoir Suisse**, Presses polytechniques et universitaires romandes, **2011**, 143 p., ISBN 9-78-2880-749385

4/ CASE STUDIES 1 : Electrochemical sensors development

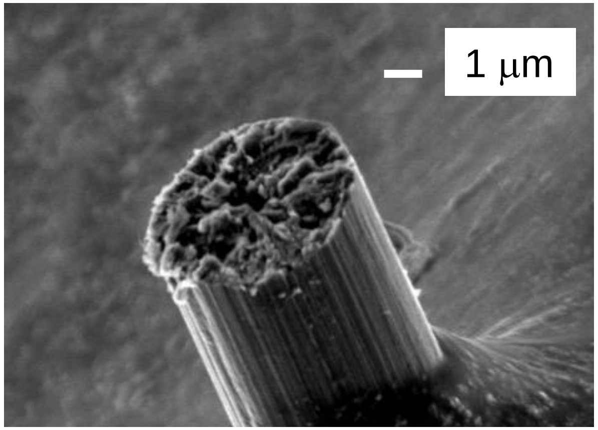
UME AND CPE SENSORS DEDICATED TO ORGANIC MICROPOLLUTANTS

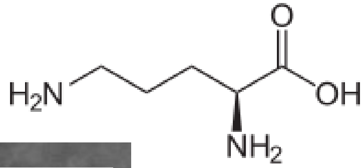
Analyzes of Molecules of Biological and Environmental Interests in my team (Hospital center Angers)

NO



Ultra-microelectrode (**UME**) with C fiber





Ornithine

MPT

PNP

phenol

PAP

4-HBz

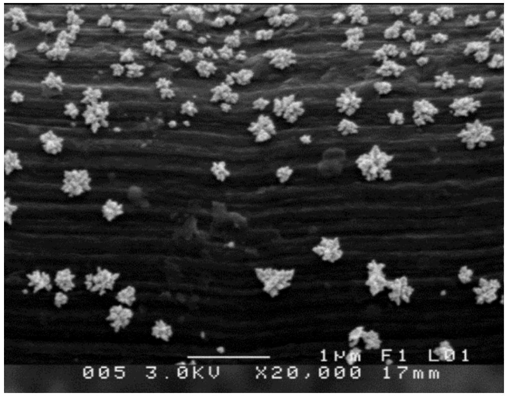
DCF

APAP

HQ

Carbon paste electrode (CPE)

MNP **Fenitrothion**



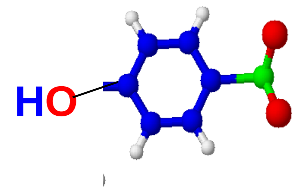
Gold nanosensors (AuNPs) on C UME

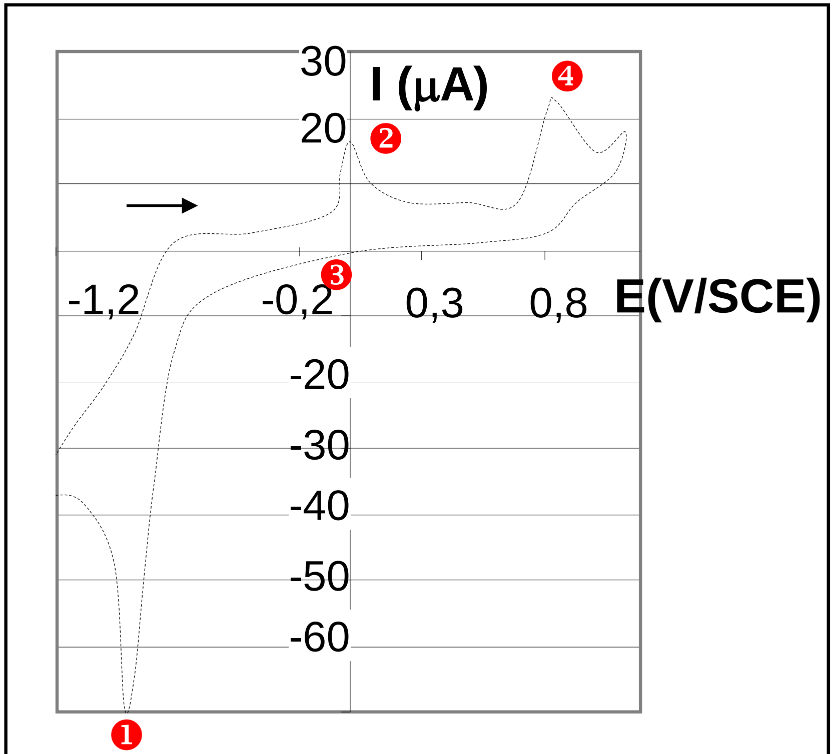
PGE (*pencil graphite electrode*)

glucose

Macroelectrodes (**GCE**, Or, Pt)

Electroactivity of PNP on GCE





Cyclic Voltammetry of PNP

- GCE
- acetate buffer (5.2, 0.1 M)
- potential scan rate : 100 mV.s^{-1}
- [PNP] = 20 mg.L^{-1}

Irreversible reduction of – NO_2
(**direct detection**):

$R\text{-}\Phi\text{-}\mathbf{NO_2} + 4\,e^- + 4\,H^+ \longrightarrow R\text{-}\Phi\text{-}\mathbf{NHOH} + H_2O$ ❶

Reversible oxidation of - NHOH
(**indirect detection**) :

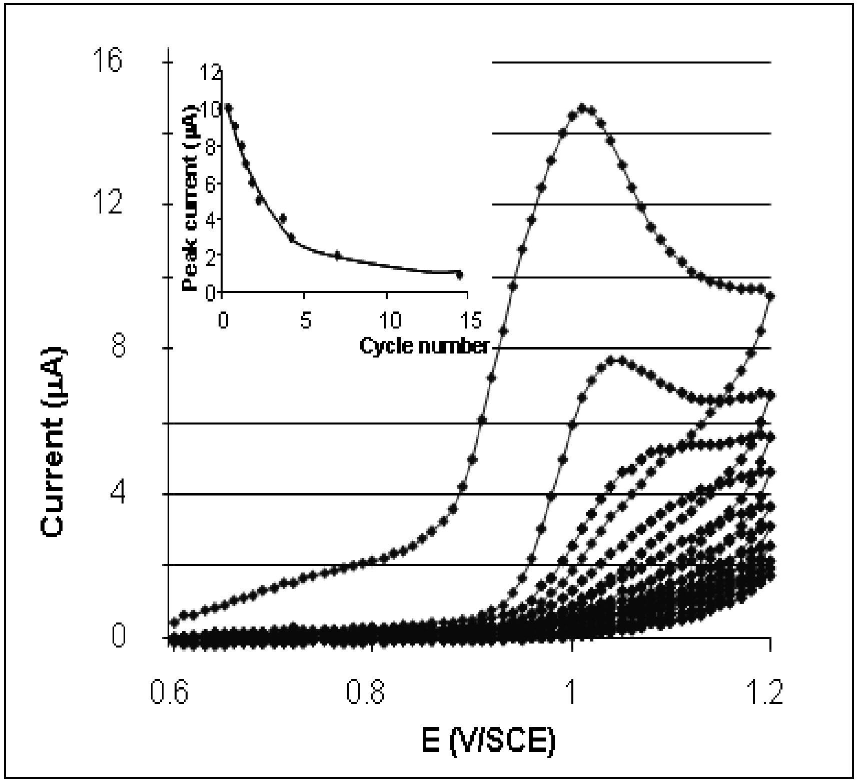
$R\text{-}\Phi\text{-}\mathbf{NHOH} \underset{❸}{\overset{❷}{\rightleftharpoons}} R\text{-}\Phi\text{-}\mathbf{NO} + 2e^- + 2H^+$

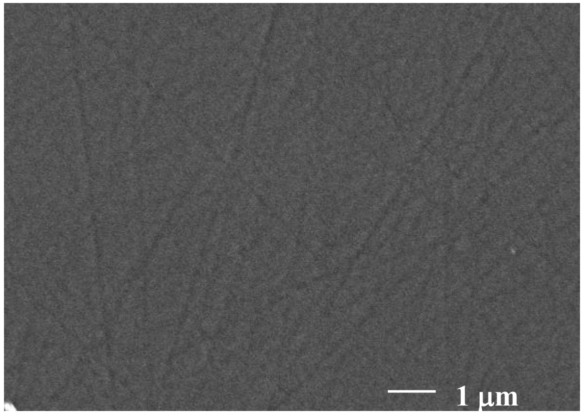
Irreversible oxidation of - Φ-OH
(**direct detection**) :

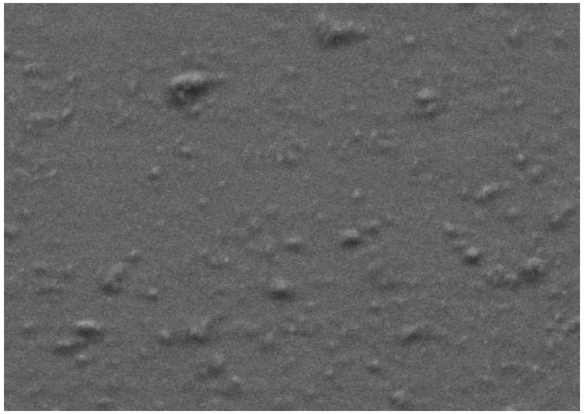
$HO\text{-}\Phi\text{-}NO_2 \longrightarrow {}^{\bullet}O\text{-}\Phi\text{-}NO_2 + H^+ + e^-$ ❹

[2] **M. Pontié *et al.*, *Electroanalysis*, 23 (2) (2011), 433.**

Electrode passivation with PNP oxidation







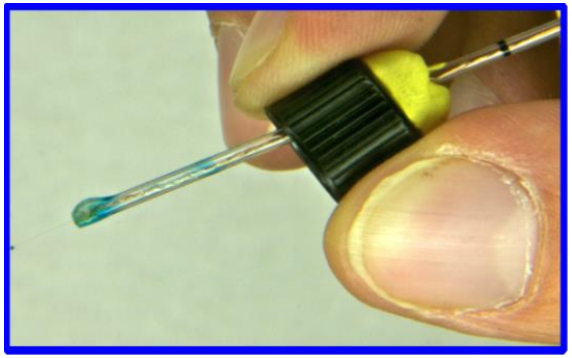
- électrolyte : ACETATE BUFFER (pH=5;2 ; 0;1M)
- SCAN RATE : 100 mV.s^{-1}
- [PNP] = 100 mg.L^{-1} (5.10^{-4} mol.L^{-1})

BE CAREFULL WITH THE FORMATION OF POLYPHENOL FILM !

[3] M Pontié, G Thouand, F De Nardi, I Tapsoba, S Lherbette
Electroanalysis 23 (7), 2011, 1579-1584

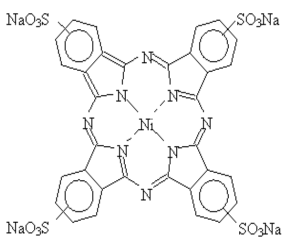
Improving the performances of UMEs' : PNP case

- **1-UME elaboration + quality control**

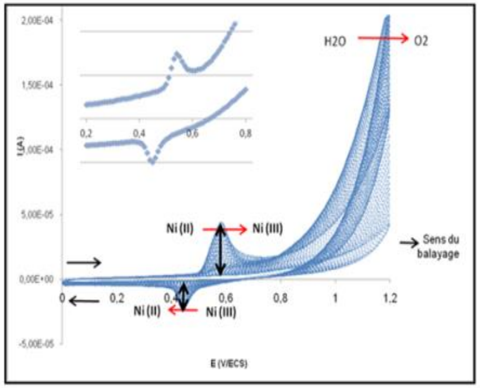


« Homemade » UME

- **2- UME modification by a film of phthalocyanine (p-NiTSPc)**

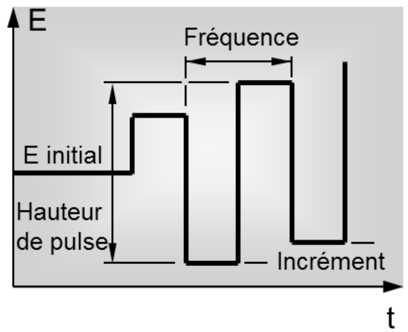


NiTsPc



Alcaline electrodeposition pH = 12

- **3- Square wave voltammetry**

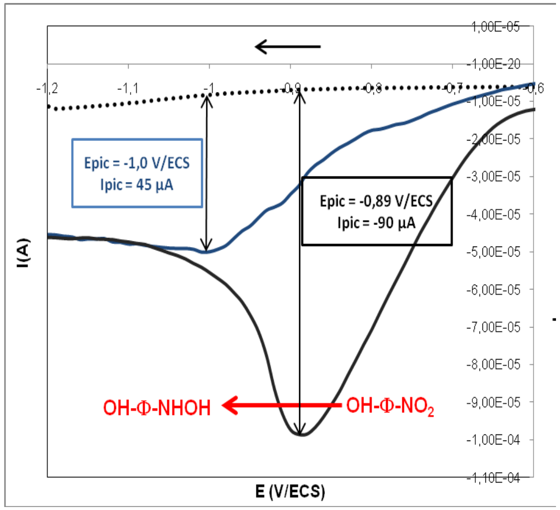


E initial : -0.2 V/ECS
Frequency : 60 Hz,
Pulse height: 90 mV
Potential incres.: 20 mV

Decreased the capacitive current

- **4- PNP analysis**

HO-Φ-NO$_2$ + 4 e$^-$ + 4 H$^+$ ⟶ **HO-Φ-NHOH** + H_2O ❶



- · · baseline
— no **p-NiTsPc**
— With **p-NiTsPc**

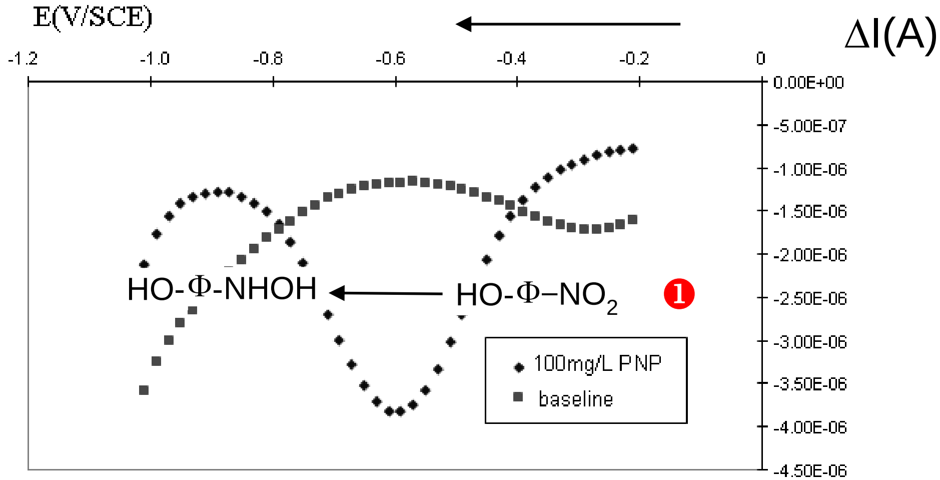
Electrocatalytic effect

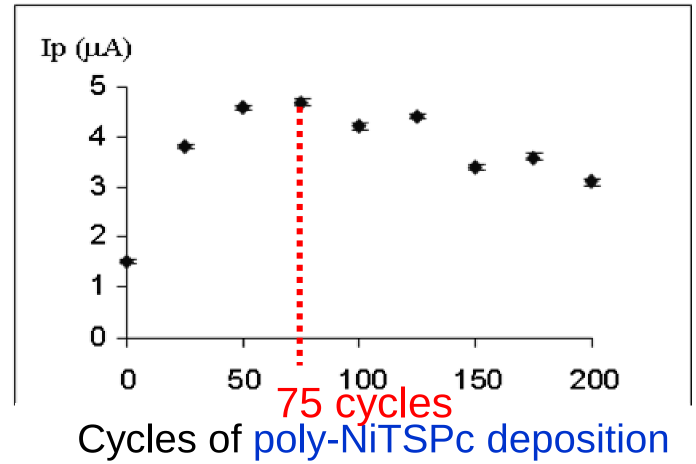
5-Higher sensitivity

UME :
C/p-NiTsPc

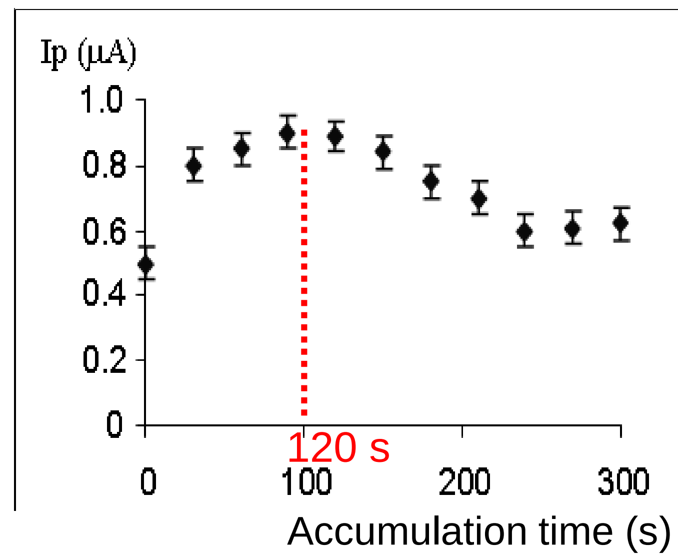
SWV

E initial : -0.2 V/ECS
Frequency : 60 Hz
Pulse height : 90 mV
Pot. Increm. : 20 mV





Operating conditions	LOD (μg/L ± 0,05)
C cleaned	100.00
C/**poly-NiTSPc** (75) No accum. time	25.00
C/**poly-NiTSPc** (75) **2 min. of accum.**	**0.10**



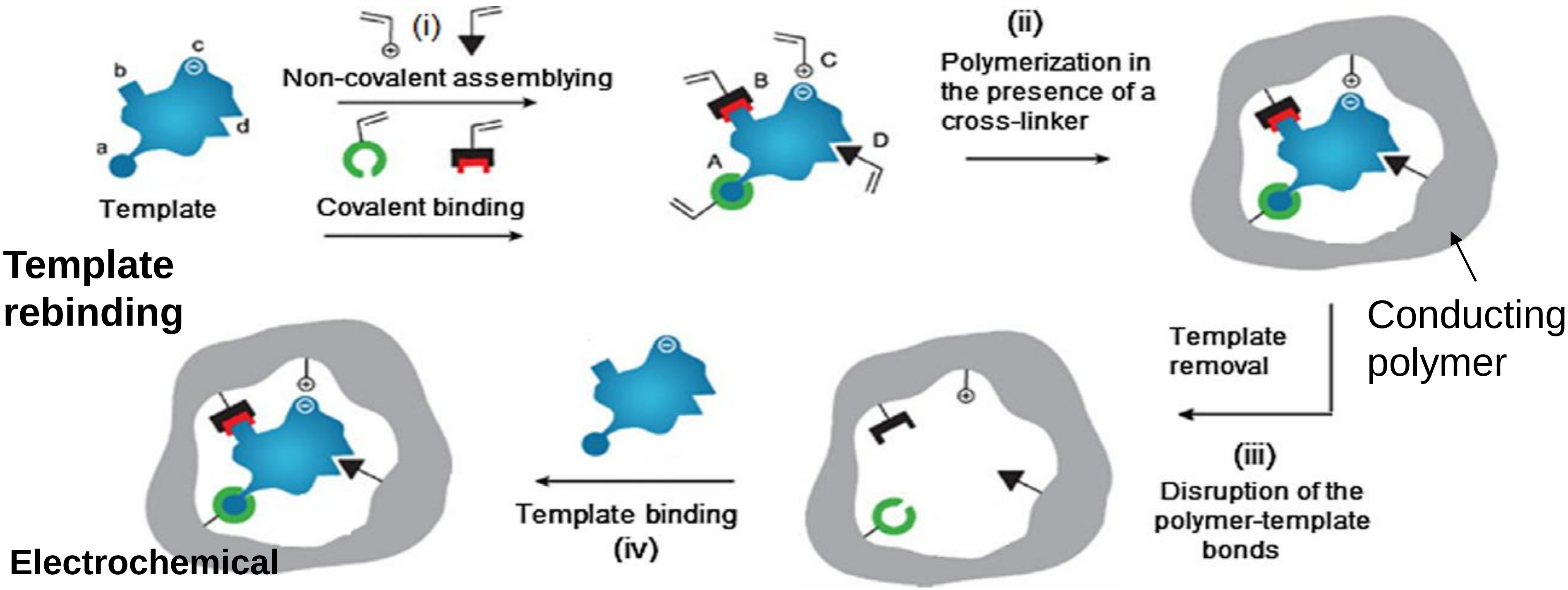
[2] **M. Pontié *et al.*, *Electroanalysis*, 23 (2) (2011), 433.**

6- Analyzes comparison between GC / MS and modified UME of estuarine and surface waters

	Laboratories and Analytical methods	LD2H GC/MS^2 (µg/L)	UME (µg/L)	C_0 (weighted) (µg/L)
	PNP Estuarine Surface (dam)	 114.5 ND	 117±6 106±6	 108±6 104±6
3 Samples	MPT Estuarine Surface (dam)	(GC/MS^2) 93.8 103.8	 96±3 114 ±3	 120±6 120±6

*3 essays by samples

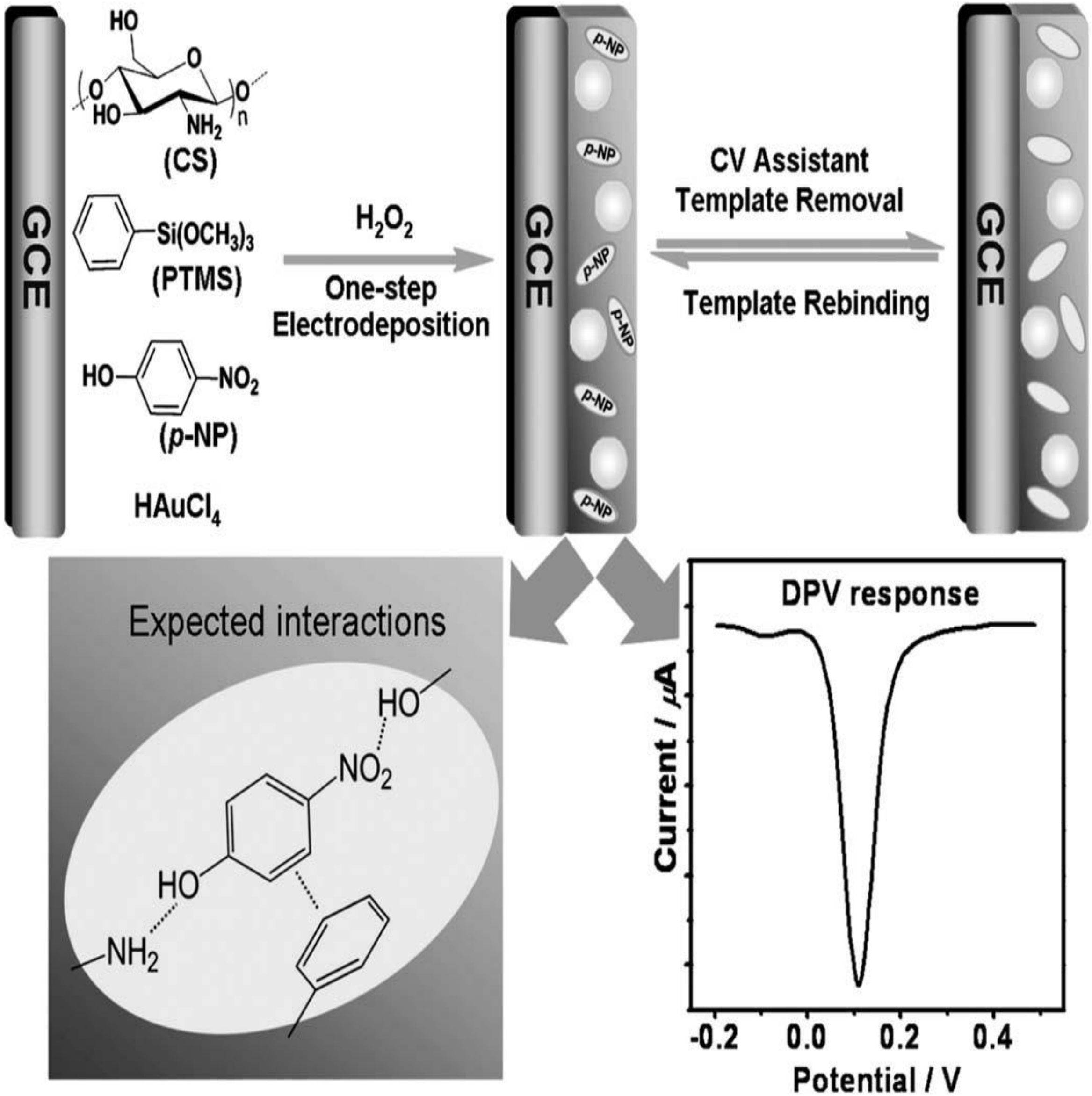
7- Improvement of the selectivity by the development of a MIP (= *molecular Imprinted Polymer*)



Electrochemical transduction
(for example)

from [4] P .S. SHARMA et al. *Trends in Analytical* **Chemistry**, (2012) 234, 59-77

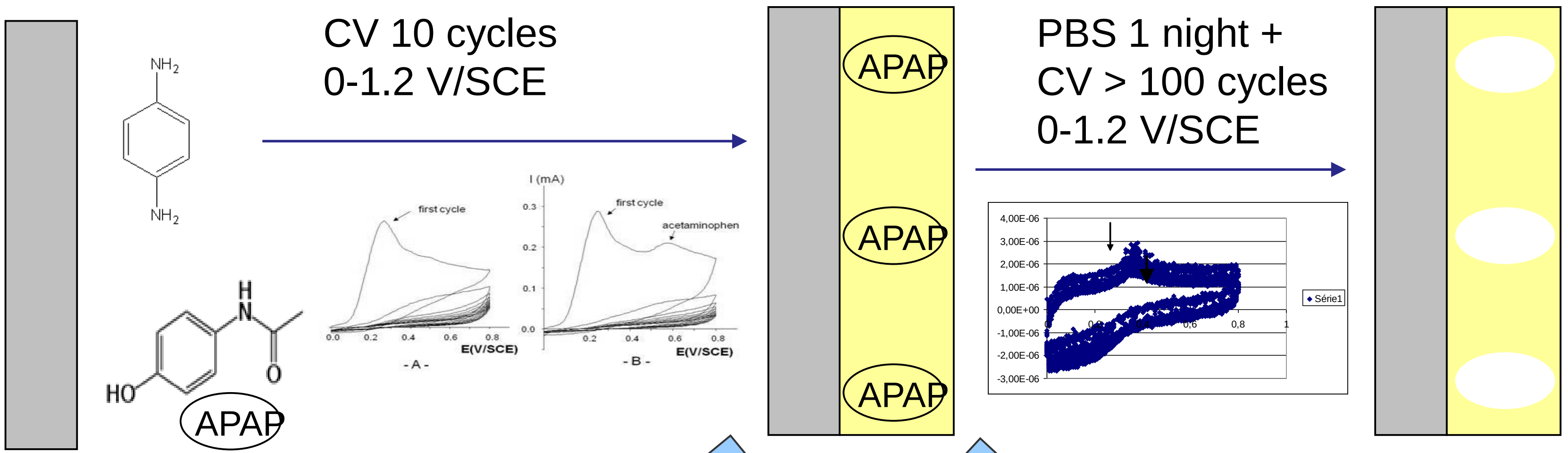
MIP dedicated to PNP



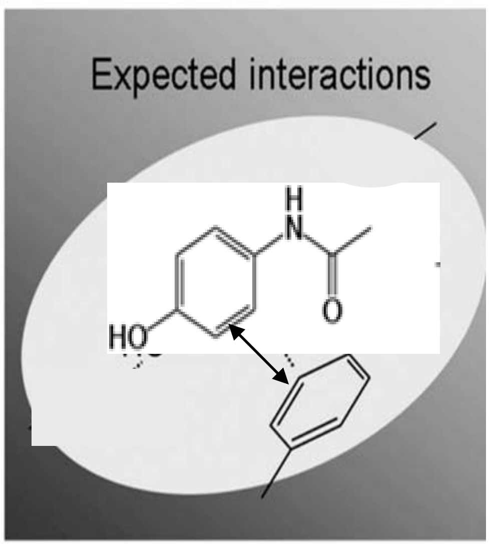
Schematic representation of the fabrication protocol of the p-NP imprinting and imprinted CS/PTMS/AuNPs/GCE for sensing p-NP. The one-step electrodeposition of the hybrid film on GCE was triggered by applying an optimal potential at -0.30 V vs. SCE for 300 s. The expected interactions in the recognition process involve hydrogen bonding and p–p stacking. The characteristic DPV response to p-NP locates at the **oxidation potential at +0.12 V vs. SCE** under the measurement conditions.

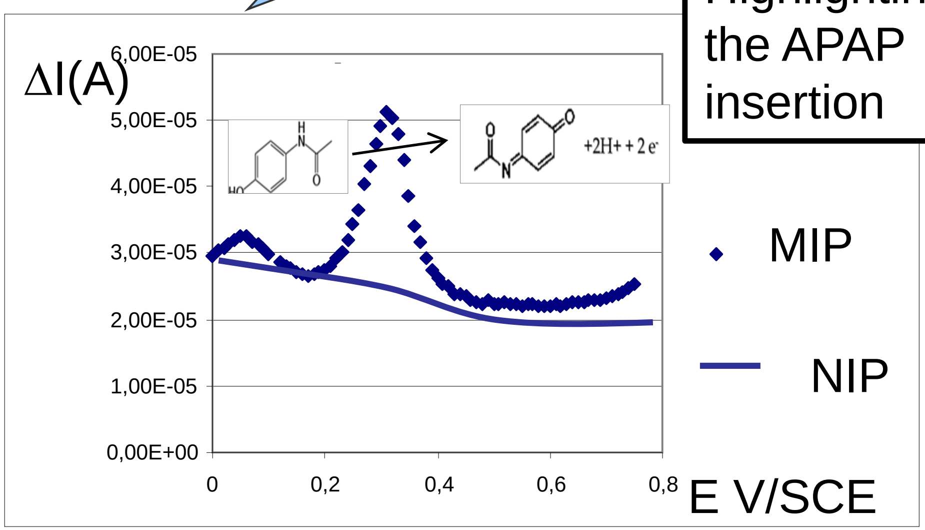
from [4] P .S. SHARMA et al. *Trends in Analytical* **Chemistry**, (2012) 234, 59-77

MIP dedicated to acetaminophen



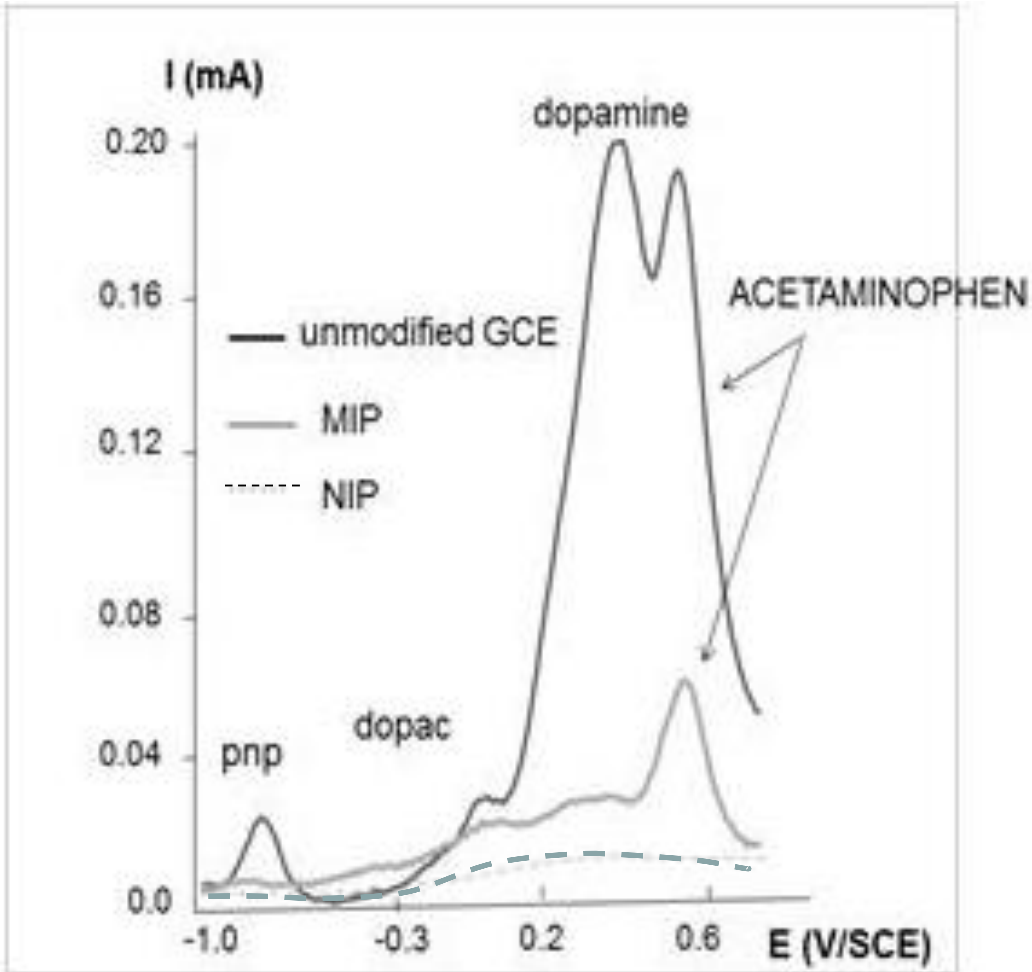
MM : 151.2 g/mol





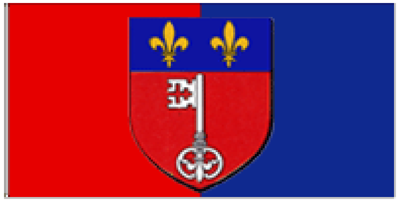
Highlighting the APAP insertion

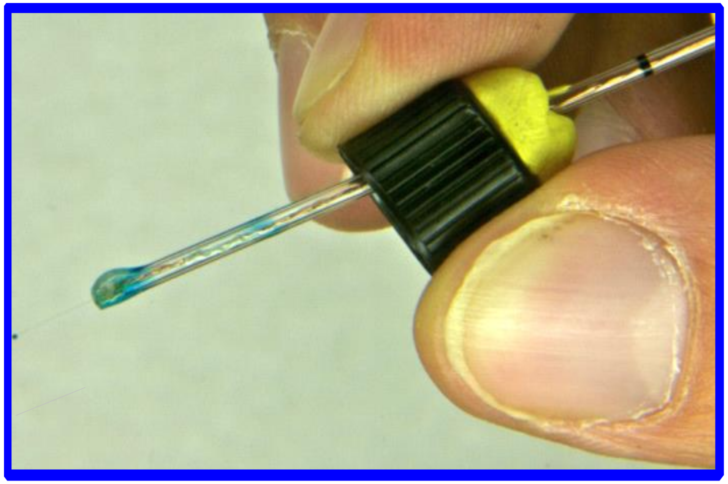
Interferences with ACETAMINOPHEN

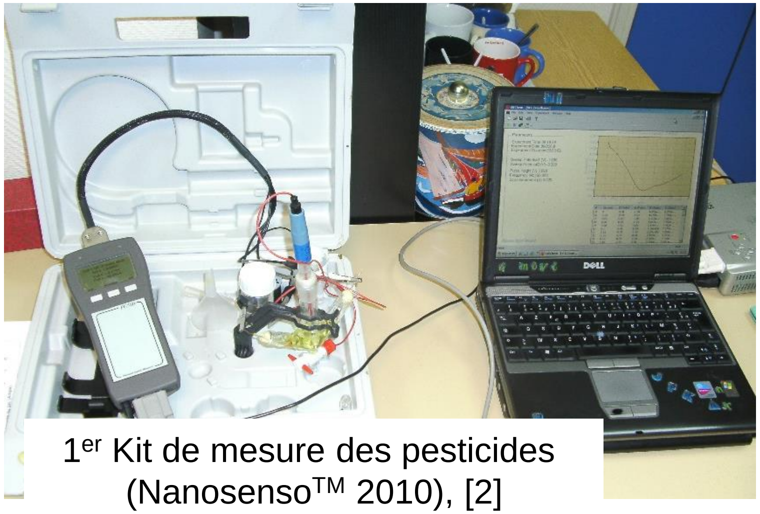


[5] **M. Pontié et coll.** ***Research and Reviews in Electrochemistry*****, vol. 8 2018, 1-10**

1er « *Homemade* » pesticide UME kit

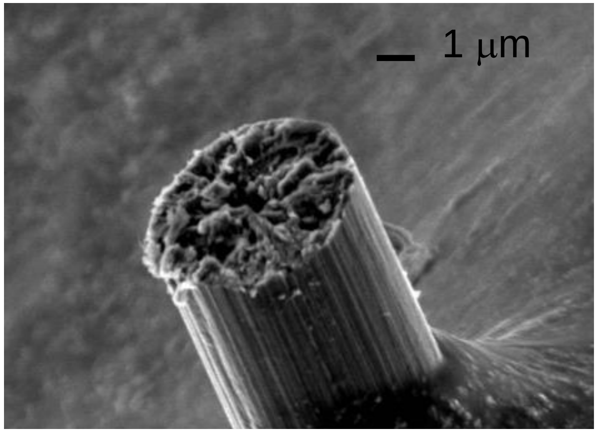






1er Kit de mesure des pesticides (Nanosenso™ 2010), [2]

made in Angers



[6] M. Pontié, « Techniques récentes en Analyse de l'Environnement et des Milieux Biologiques », Les Techniques de l'Ingénieur, IN 140, **2010**

CPE acetaminophen sensitive sensor cellulose-based

Chitosan,
Clays,
CNanotube,
Graphen,
, …

Materials used to sensors/biosensors electrodes

LCM* as new sensor materials ?

Improving sensitives and selectives of the (bio)sensors

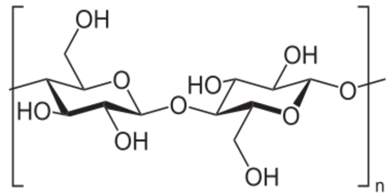
*LCM = ligno-cellulosic matter

Ecofriendly sensors, low cost analysis of drugs sold individually in the streets in Cameroon

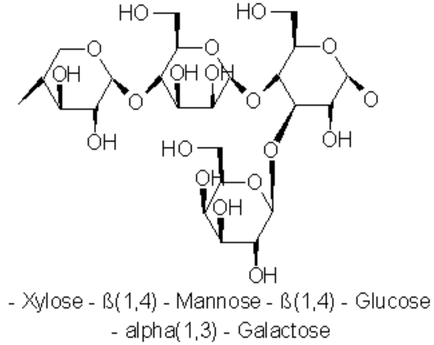
Origalys
LCA LABORATOIRE DE CHIMIE AGRO-INDUSTRIELLE
université angers
Lachinge Dschang, Cameroon

LIGNO-CELLULOSIC MATERIALS

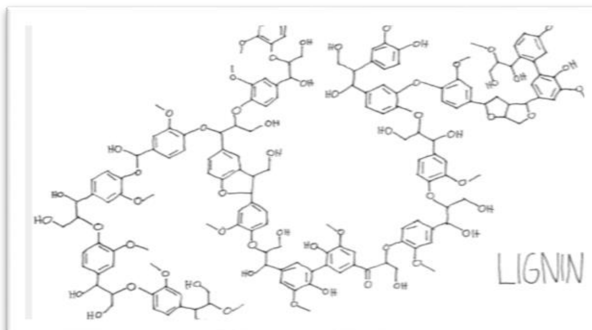
Coffee
Husk (CH) from Cameroon



cellulose **(40%)**



Hemi-cellulose (≈ 35%)



Lignin (≈ 17%)

Extractibles matters : polyphenols, phenols, pectins, sugars, esters of fatty acids, alcaloids, steroids…

(2 % to 8% of dry matter)

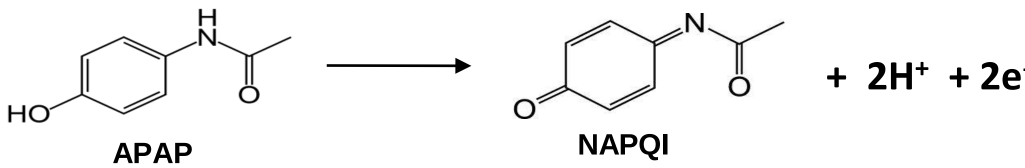
Minerals (≈ 2%)

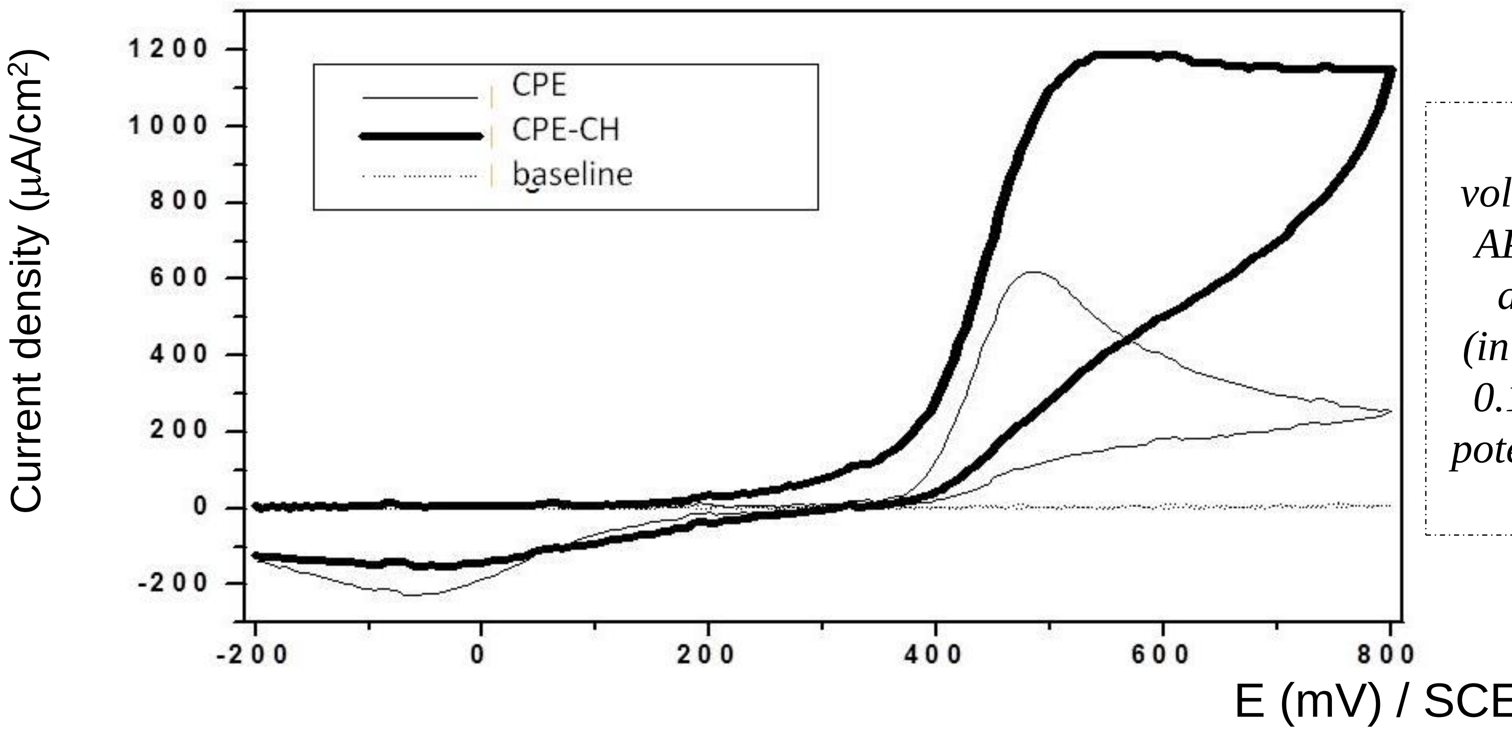
fraction size
< 100 µm

55% cellulose, 5% hemi-cellulose, 9% lignin, 31% others (not determined)

see [7] **Mbokou S.F.** ***et al. Inter. J. Electroch.*** **Vol. 1 (2016) 1-10**

ACETAMINOPHEN (APAP) ELECTROACTIVITY



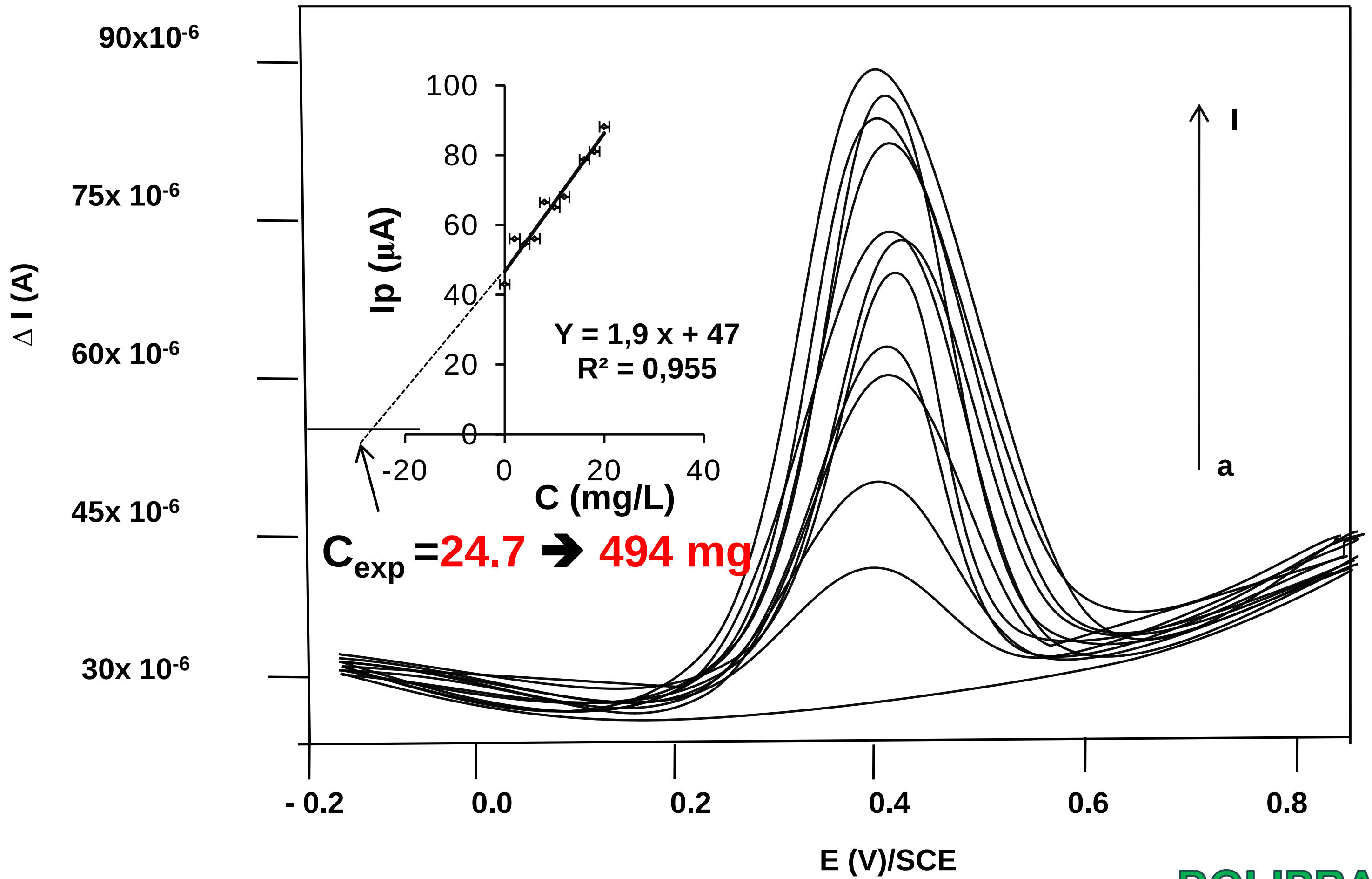


*Cyclic voltammogram of APAP with CPE and CPE-CH (in PBS, pH=7.4, 0.1 M, **75 mg/L**, potential scan rate 100 mV/s)*

Direct oxydation at a potential **: # 500 mV / SCE**

CH modification double the peak intensity

CPE-CH validation with APAP commercialized tablets



DOLIPRANE 500©

CPE-CH validation for DOLIPRANEs 500/1000 tablets

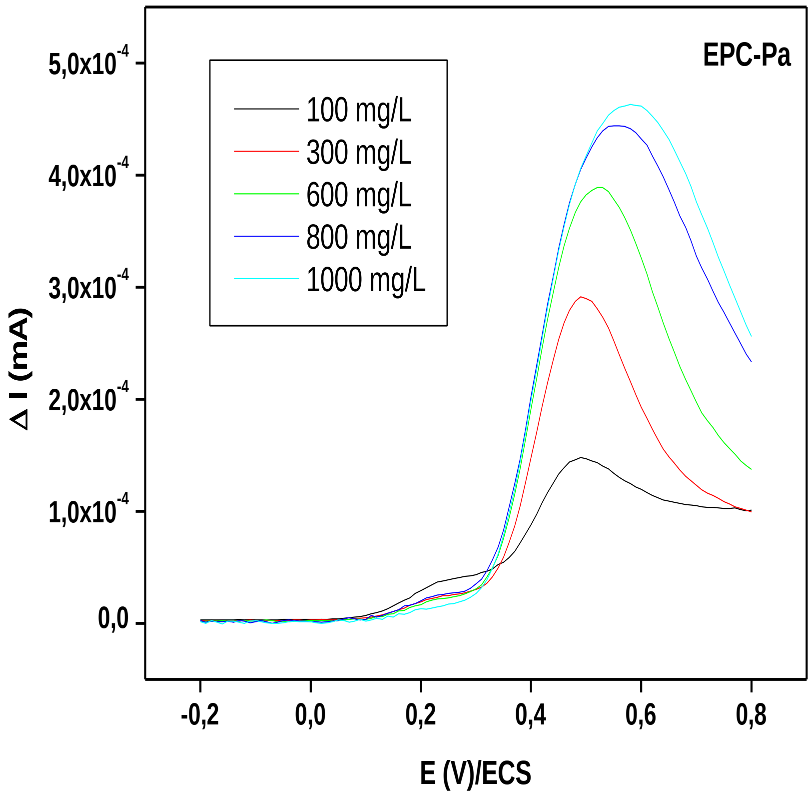
- Doliprane 500 (**Regulation** : 500 ± **15 mg**)
- Doliprane 1000 (**Regulation** : 1000 ± **30 mg**)

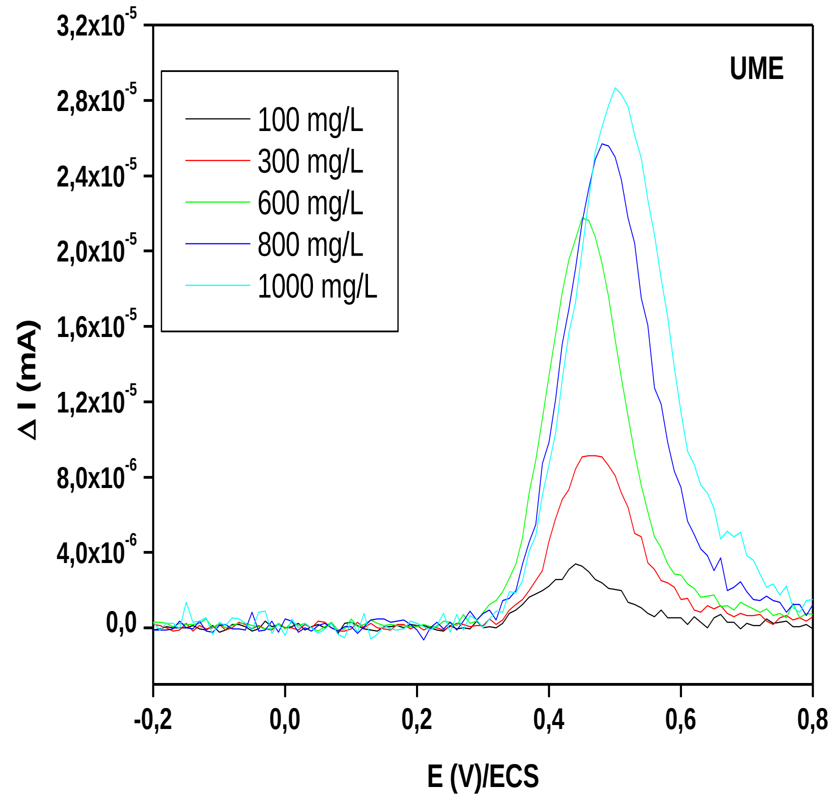
3 tablets tested

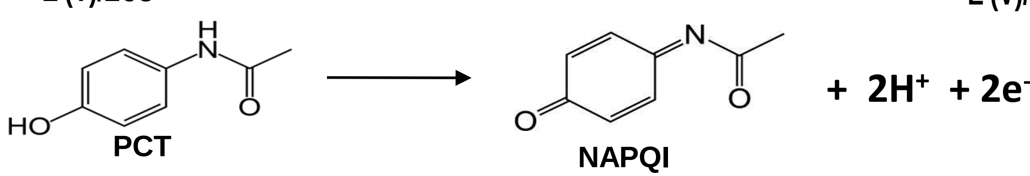
Doliprane 500© (weighted tablet # 600 mg)	slope(µA M^{-1})	1.9
	R^2	0.96
	C_0 (mg/L)	**24.7±0.5**
	Exp. APAP in tablets (mg)	**494 ± 9**
	Recovery (%)	97-101
Doliprane 1000© (weighted tablet # 1080 mg)	slope	2.1
	R^2	0.95
	C_0 (mg/L)	51.0±0.5
	Exp. APAP in tablets (mg)	**1020 ± 20**
	Recovery (%)	102-105

Recovery=($m_{exp.}$/m_{theory}) * 100

COMPARISON UME AND CPE vs APAP concentration

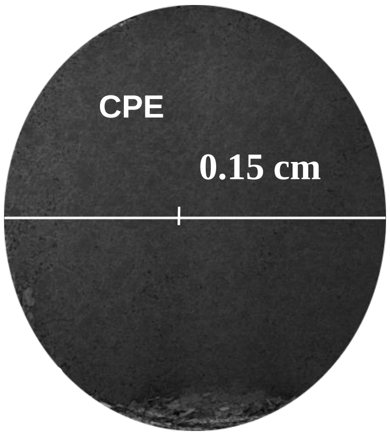


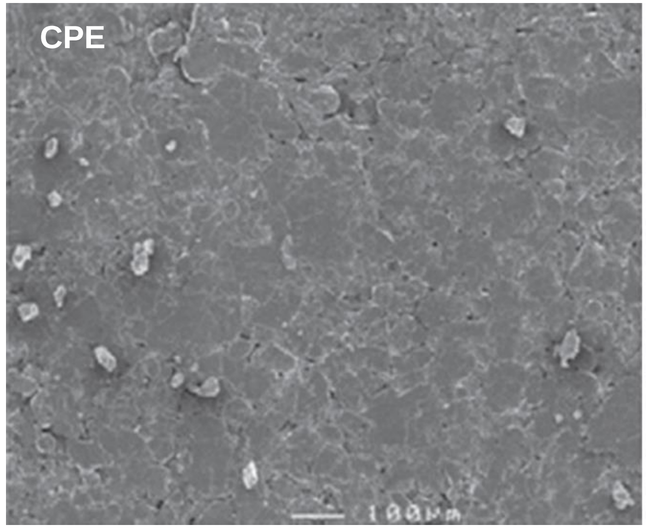


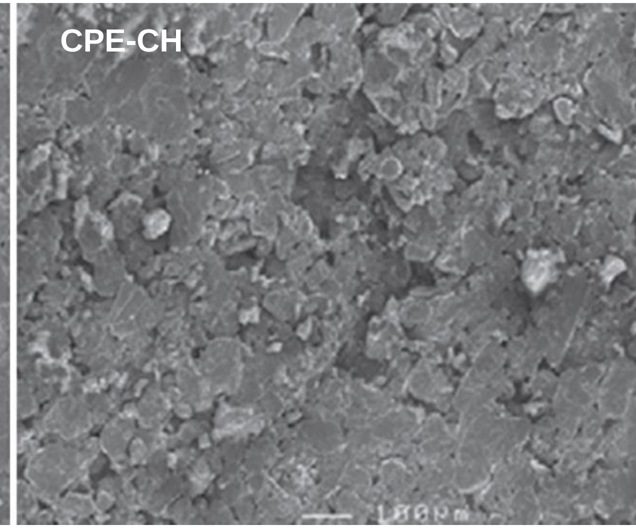


Saturation problem observed with CPE-CH from 600 mg/L, which is not the case of UME. UME is better adapted to "strong" concentration

SEM analysis of CPEs modified and unmodified



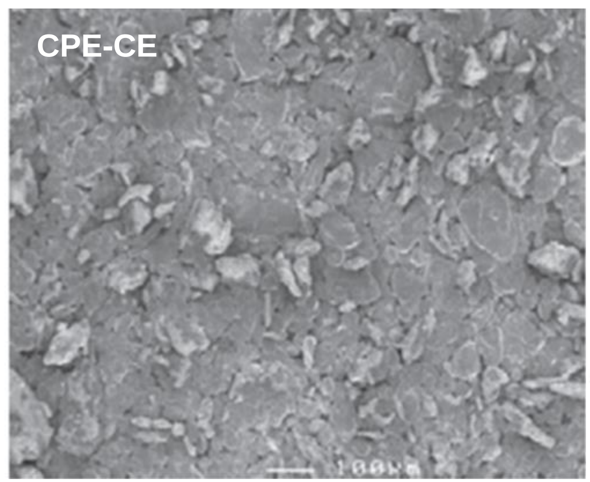


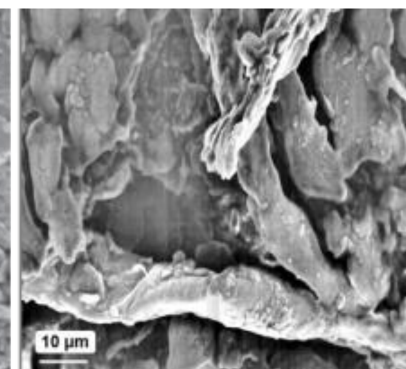


(magnification: x15)

Electrodes diameter = **3 mm**

$S_{geom} = \pi R^2 = \mathbf{0.071\ cm^2}$
with R = 0.15 cm





cellulose fibers length between ***0.02-0.15 mm (Fluka)***

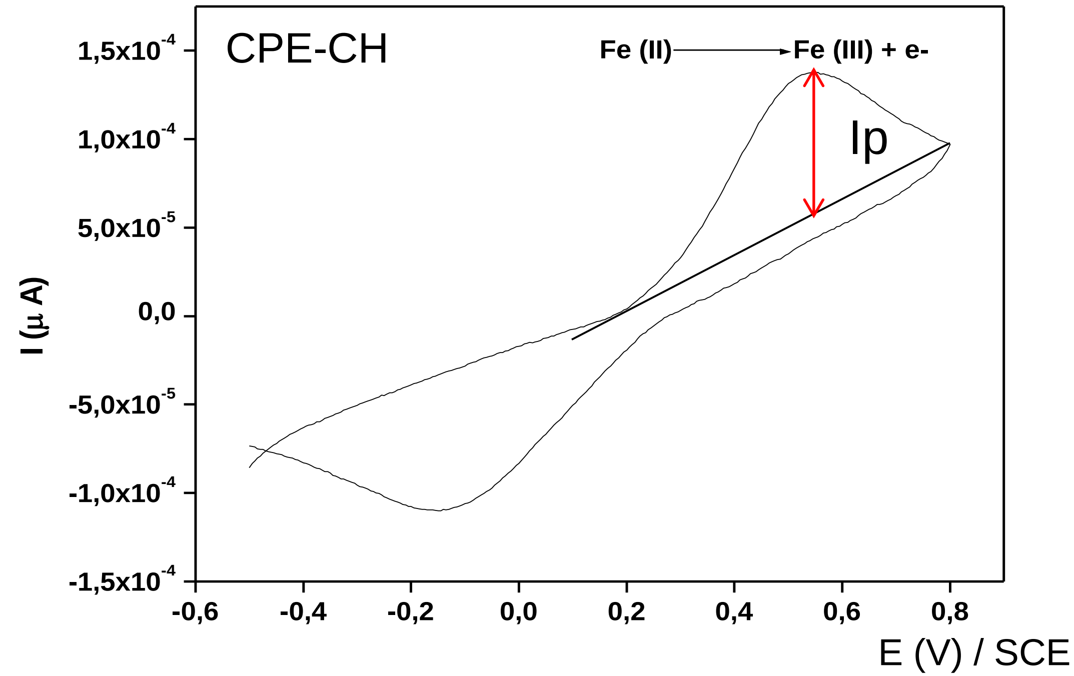
Coffee husk and cellulose particules change the morphology of CPE surface increasing the roughness

Determination of the real area with Fe(II) as a probe

Randles-Sevciks' law :

$$I_p = K\, n^{3/2}\, S\, D^{1/2}\, C\, V^{1/2}$$

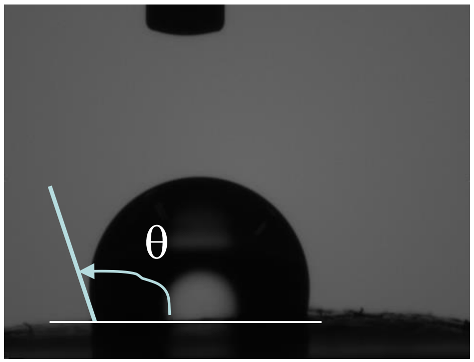
Fe(II) =Fe(III) + 1 e⁻

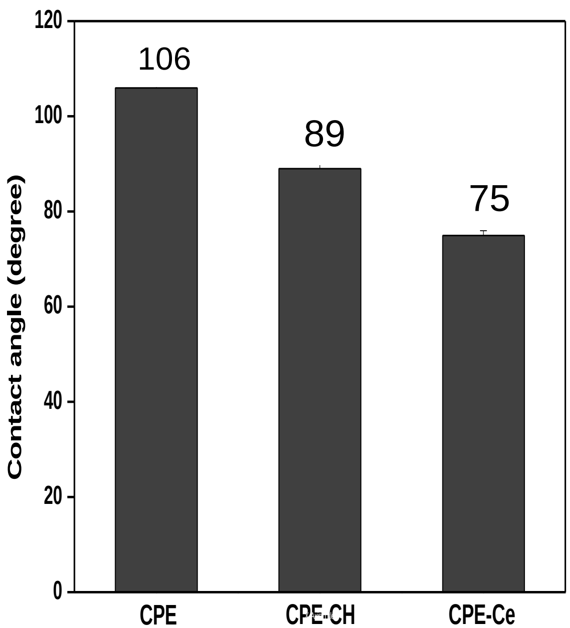


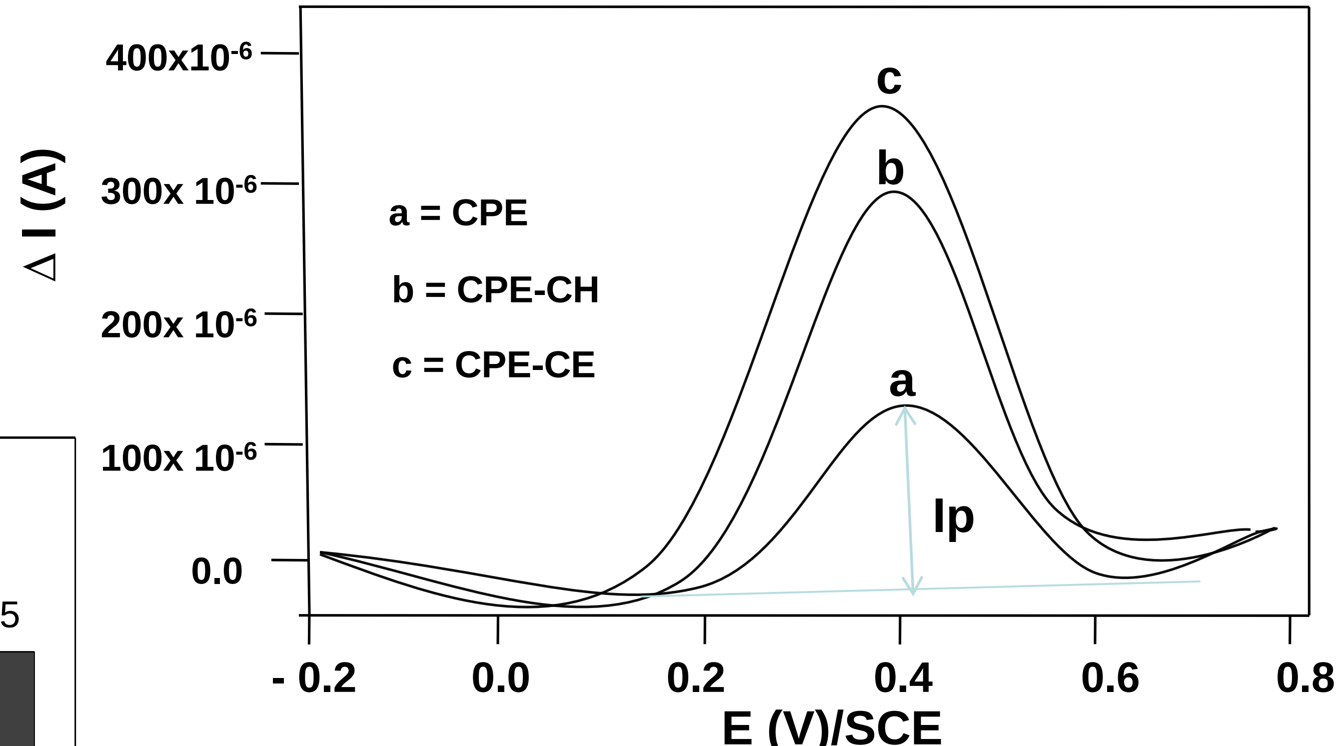
Electrodes	Geometrical area	Real area (S)
CPE	**0.071 cm²**	**0.082 cm²**
CPE-CH	0.071 cm²	**0.097 cm²**
CPE-CE	0.071 cm²	**0.141 cm²**

S (CPE-CE) > S (CPE-CH) >> S (CPE)

Correlation : sensitivity / hydrophilicity







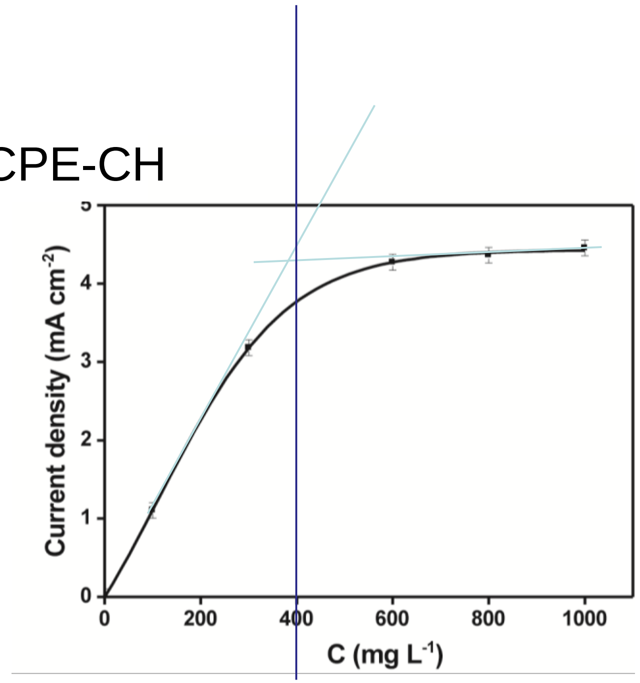
*Square wave voltamogram of APAP in PBS, pH=7.4, 0.1 M, **75 mg/L***
(pulse high : 90 mV; frequency : 400 Hz; scan Increment : 15 mV)

Correlation between hydrophilicity increasement and peak intensity

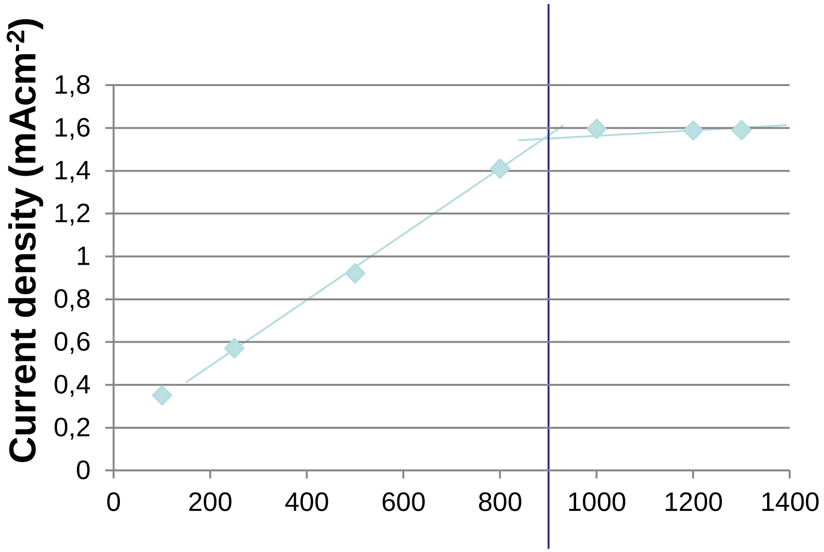
CPE-CE >> CPE-CH >> CPE

Area gain and limit of saturation for CPE-CH *vs* CPE-CE

CPE-CH



CPE-CE



Saturation : **400 mg/L** **900 mg/L**

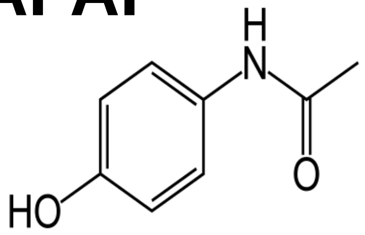
[8] Pontié, SF Mbokou, JP Bouchara, B Razafimandimby, S Egloff
Journal of Renewable Materials 6 (3), (2018) 242-250

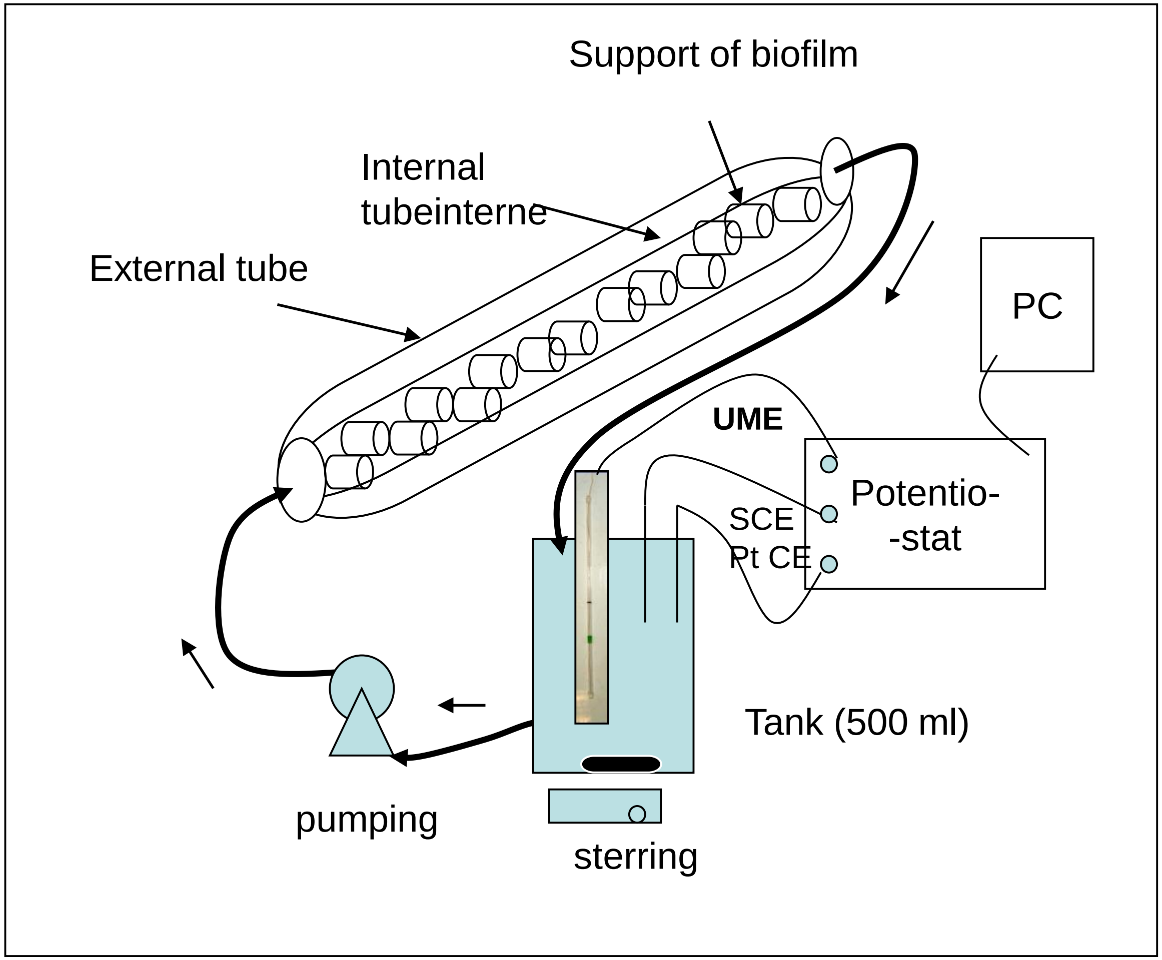
5/ CASE STUDIES 2 : Electrochemical analysis and WWT processes

- **MEMBRANE BIOREACTOR FOR APAP BIODEGRADATION**
- **STRATEGIES ANTIBIOFILMS ON UME vs CPE**

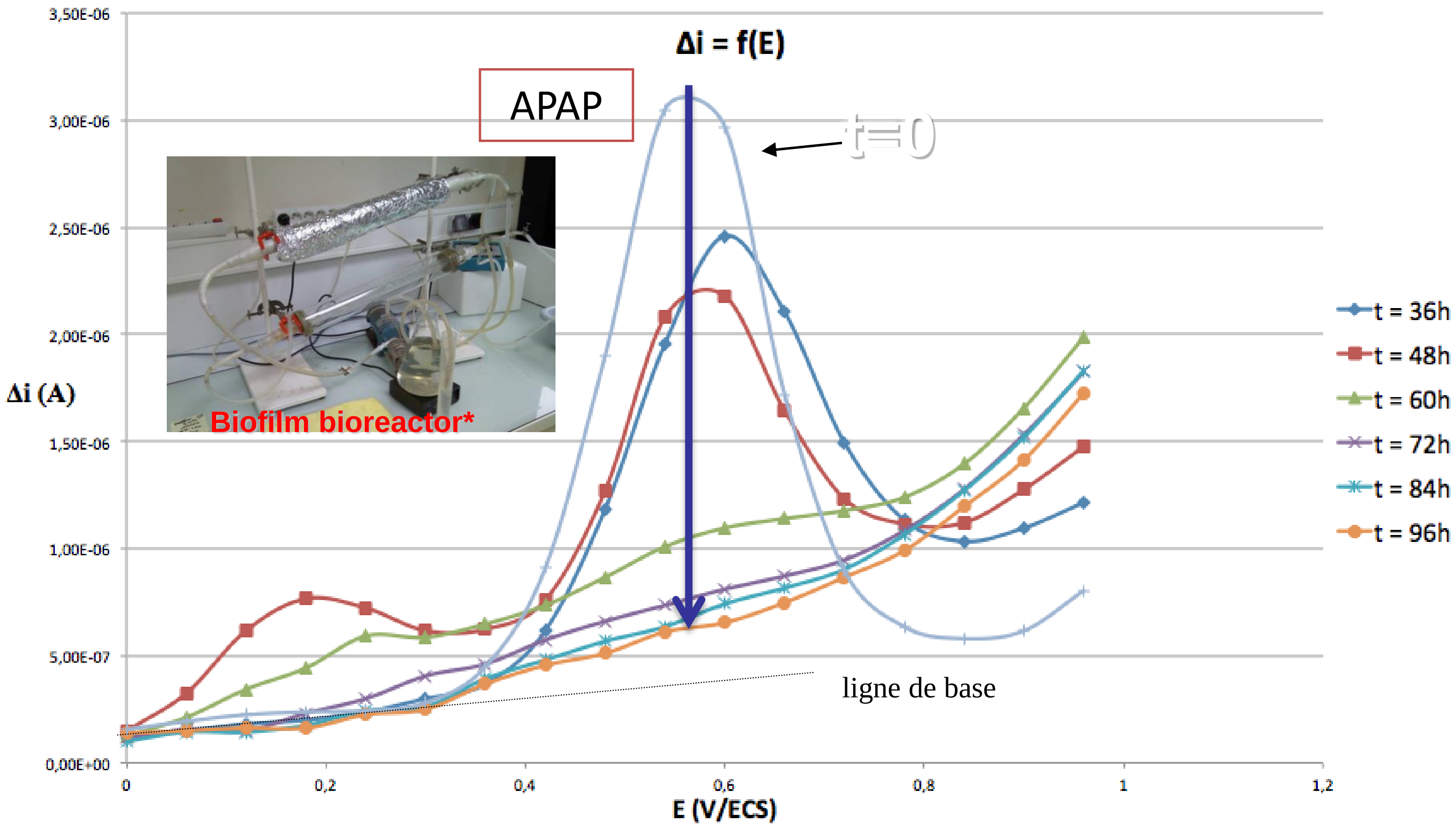
STUDY OF THE BIODEGRADATION OF APAP IN A BIOFILM BIOREACTOR

APAP





BIODEGRADATION OF APAP

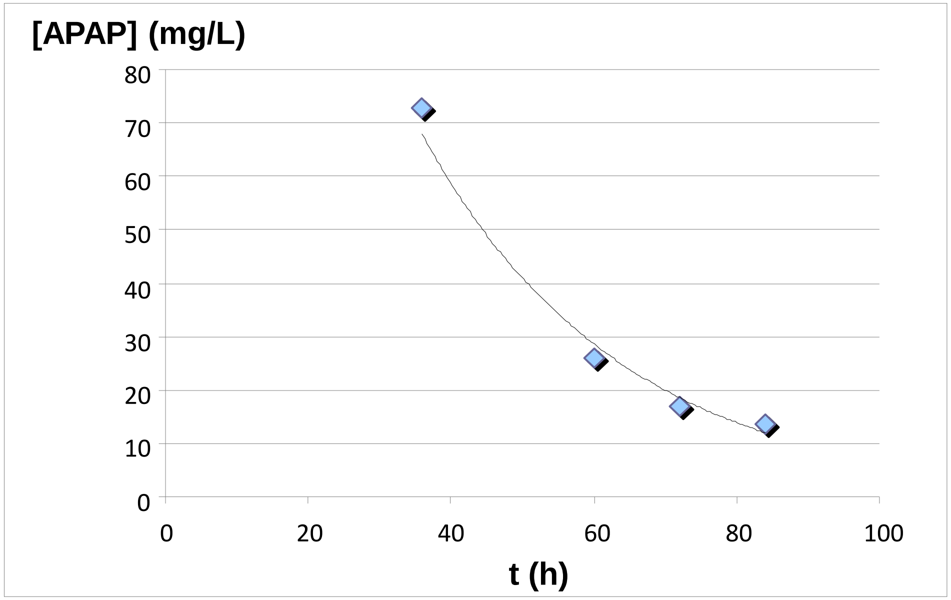


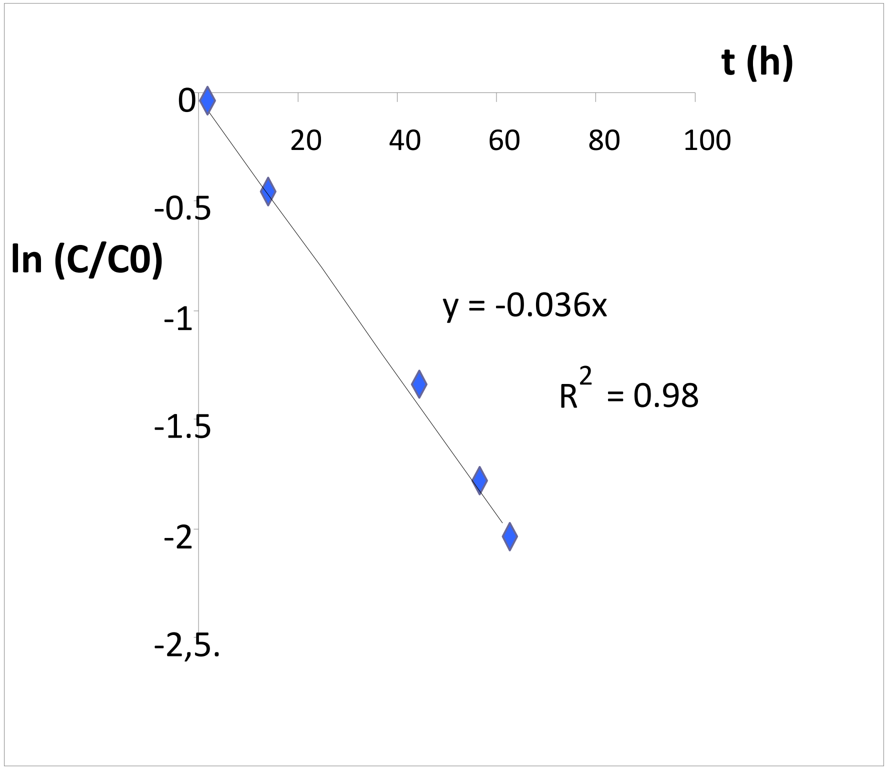
(*biofilm of 8 months
Thickness : 8.4 mm)

C_i = 100 mg/L

Conversion = 95% after 4 days

Kinetic parameters



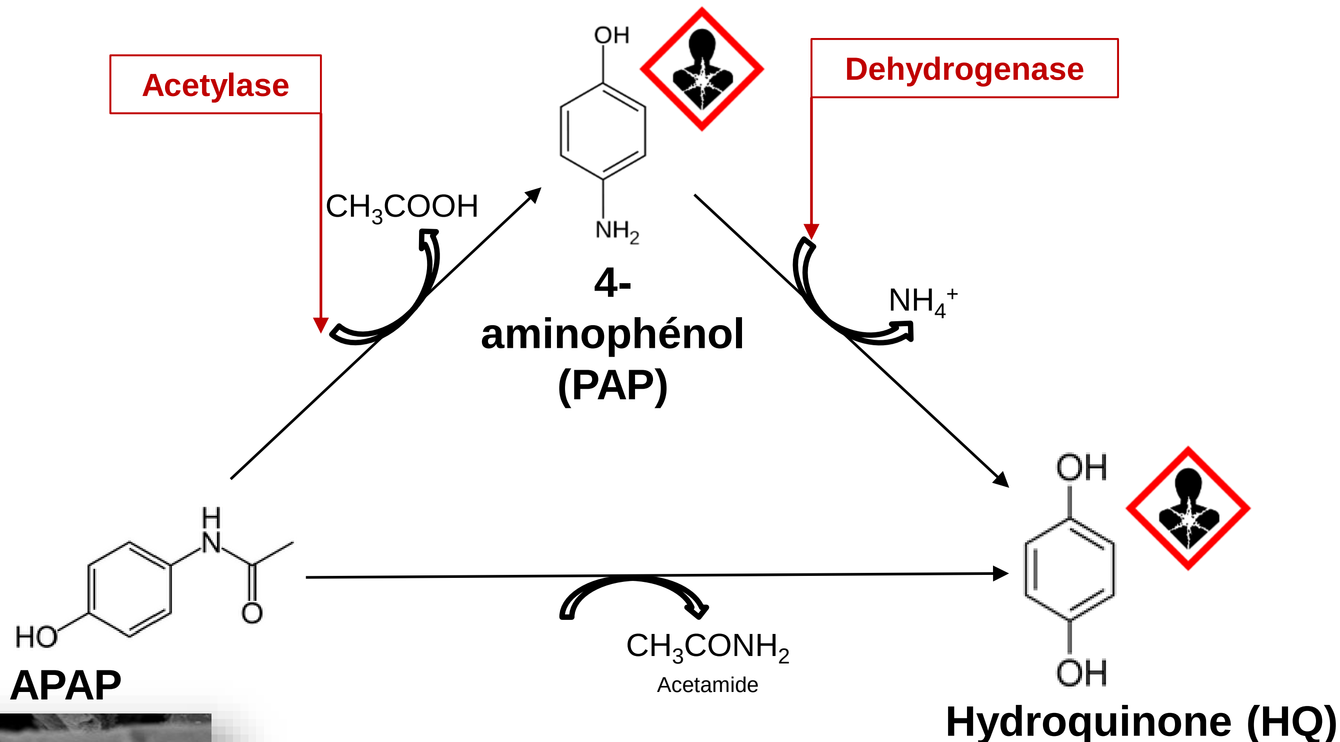


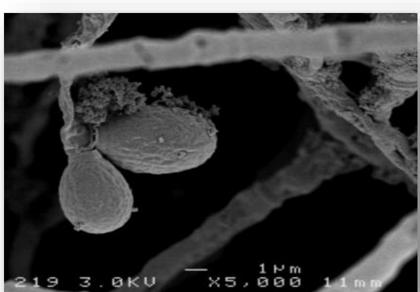
kinetic order 1 (T=20°C)

lnC/Co=-0.036.t R^2=0.96 and $t_{1/2}$=19h

Conversion = 95% after 4 days

APAP bacterial degradation by-products

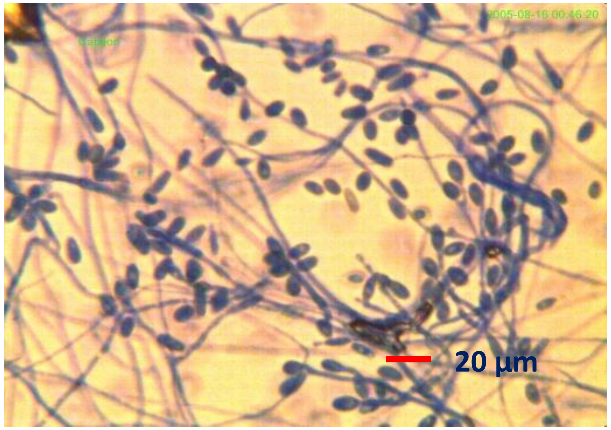




Another way : find a microorganism usable for aromatic compounds biodegradation **with no formation of toxic by-products**

[9] Zhang L *et al.*, **Appl Microbiol Biotechnol** 97 (**2013**) 3687.

Scedosporium dehoogii



Scedosporium dehoogii on YPD agar (14 days, 25^{0}C).
surface (left) and reverse (right) sides of the colony
(strain n°110 350 905)

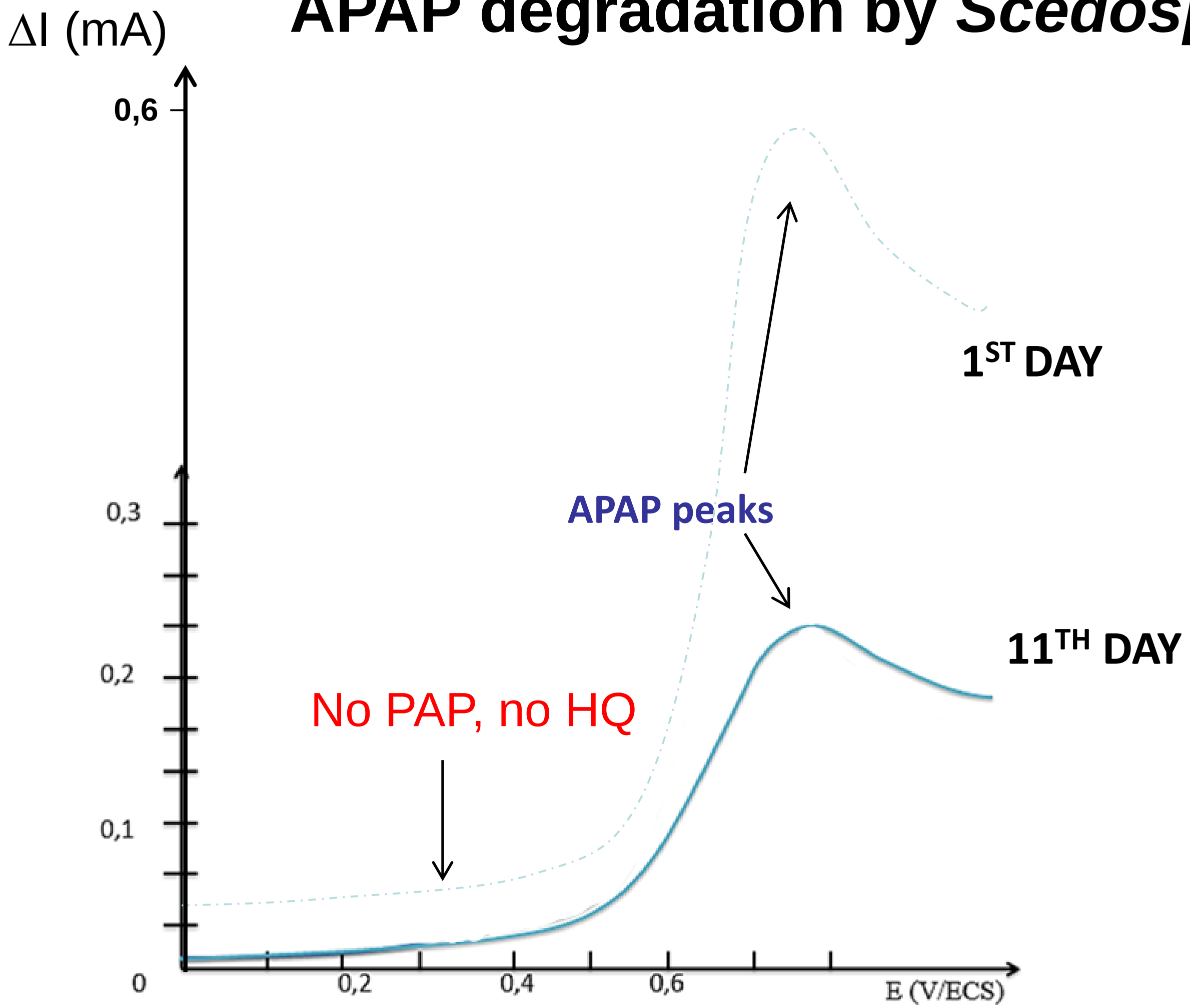
Saprophytic
Aero-anaeroby facultative
All the enzymatic equipment needed for hydrolysis of plant cell wall lignin and polysaccharides (cellulose, hemicellulose)

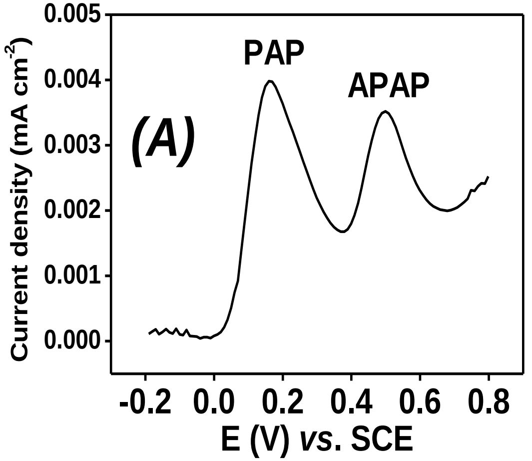
Encountered in highly polluted waters and soils (bioindicator of anthropogenic pollution)
Able to use aromatic or aliphatic compounds as sole carbon source

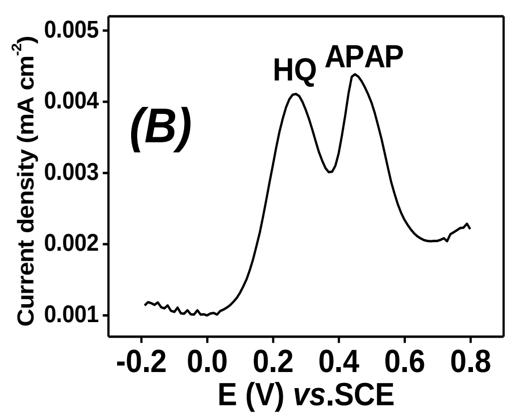
Optimal temperature 25°C but thermo-tolerant to 50°C

Several species pathogenic but not *S. dehoogii* !

APAP degradation by *Scedosporium dehoogii*



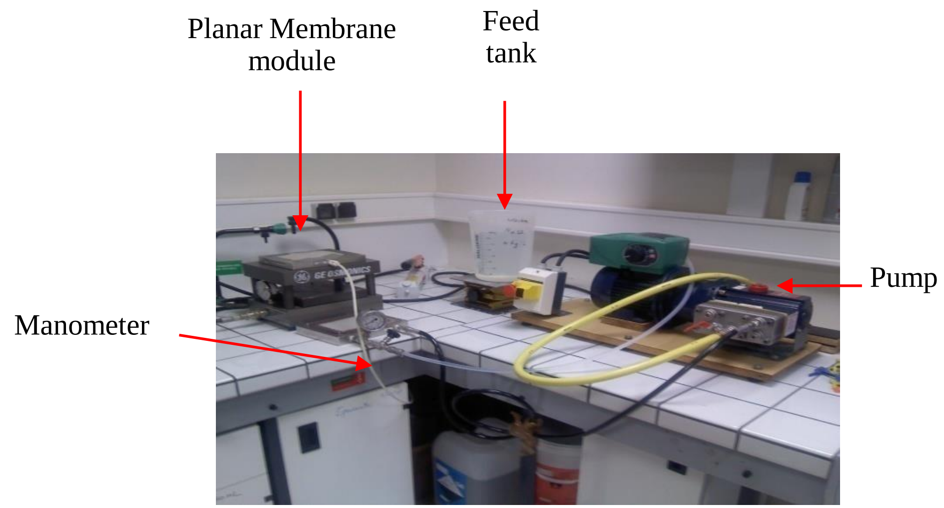




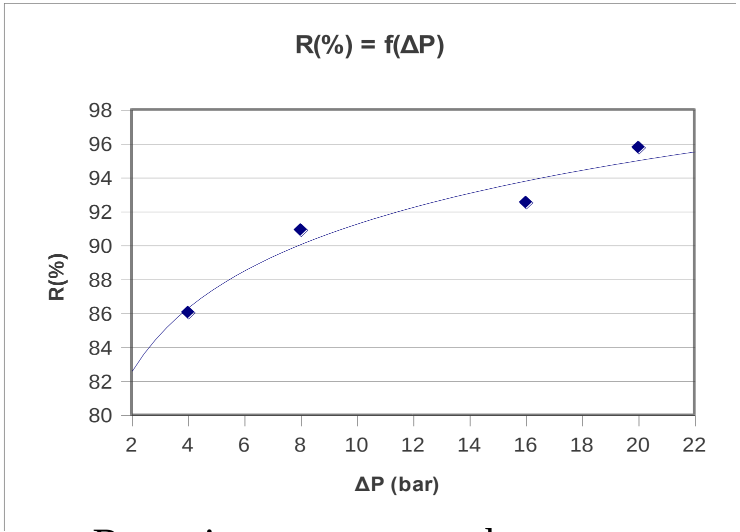
S. dehoogii is able to grow using APAP as source of carbon without toxic by-products like PAP or HQ

[10] S.F. Mbokou, I. Tonle, M. Pontié, **J Applied. Electrochem.**, 47, **2017** 273–280

NANOFILTRATION CAN ACHIEVE THE TREATMENT



NF lab scale device



Retention vs transmembrane pressure

At 20 bars, NF permeate gives **0.2 mg/L**
(regulation effluents phenol index < 0.3 mg/L)

CONCENTRATE SOLUTION MANAGED IN BIOREACTORS

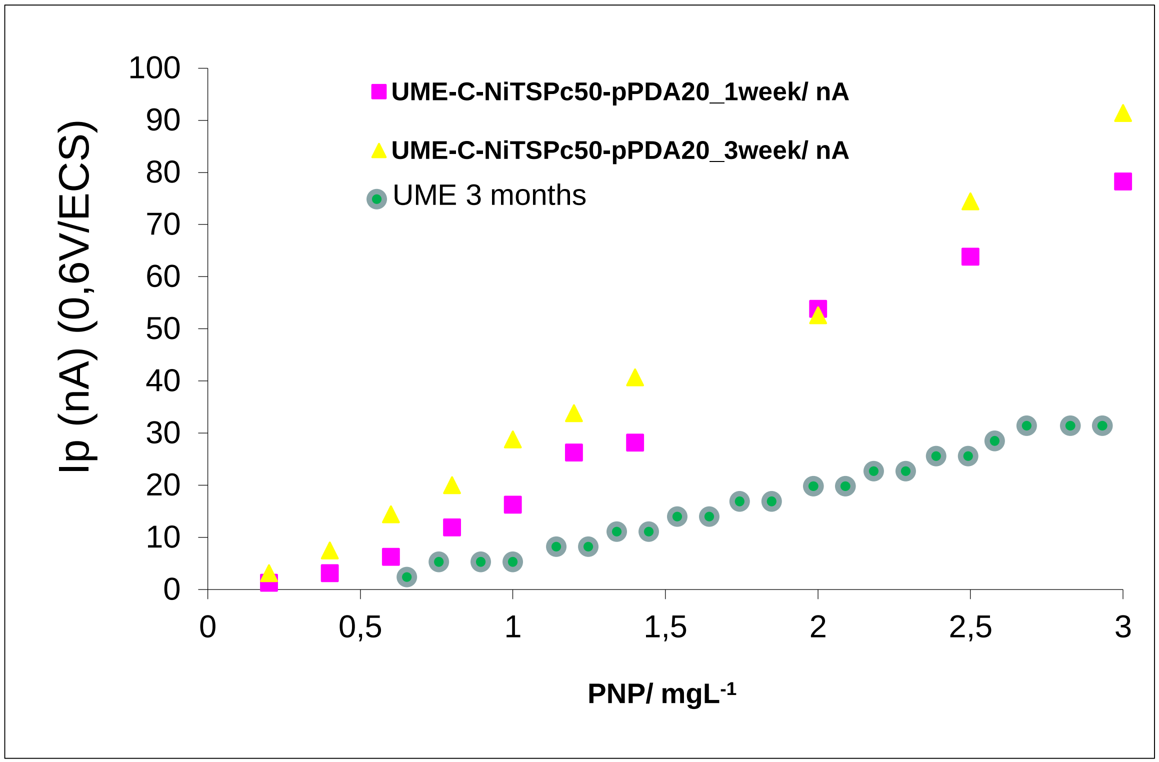
[11] Nghiem L.D., Schafer A.I., Elimelech A.M. (2005). Environmental science & technology. Vol 39. 7698-7705.

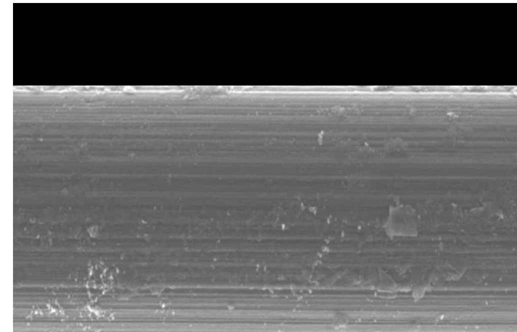
5/ CASE STUDIES 2 : Electrochemical analysis and WWT processes

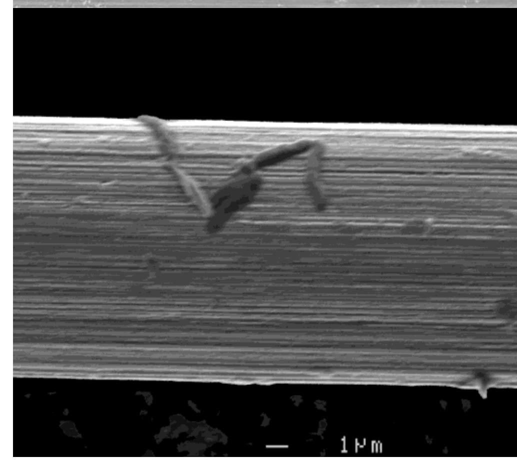
- MEMBRANE BIOREACTOR FOR APAP BIODEGRADATION

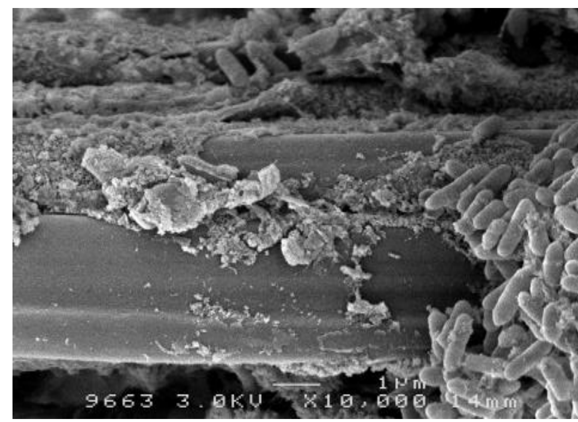
- STRATEGIES ANTIBIOFILMS ON UME vs CPE

UME stocked 3 weeks in acetate buffer (pH=5,2) at ambiant temperature and used during 3 months with real waters







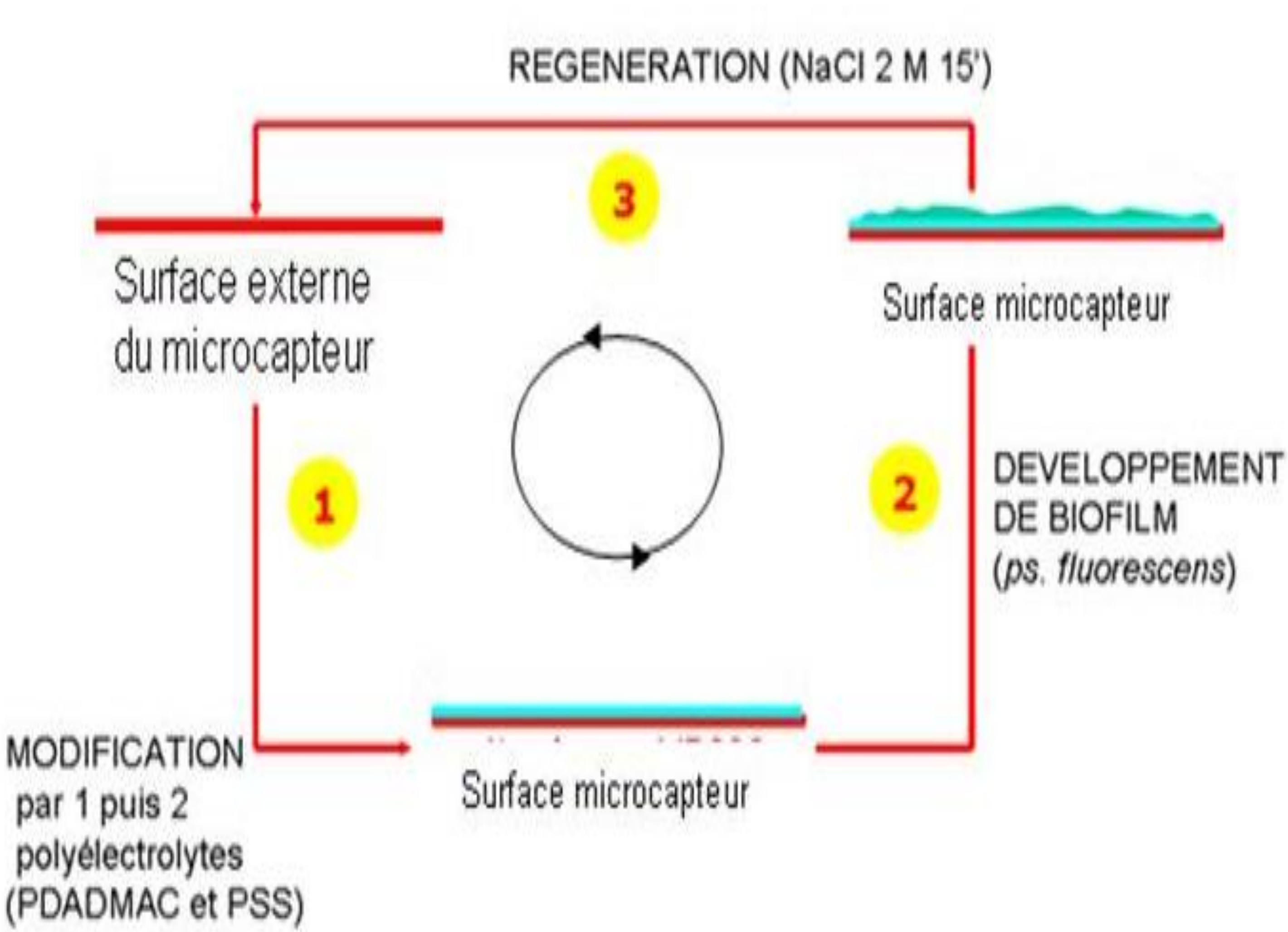


⇨ Only 5% lost of permeability + **microbial development start**

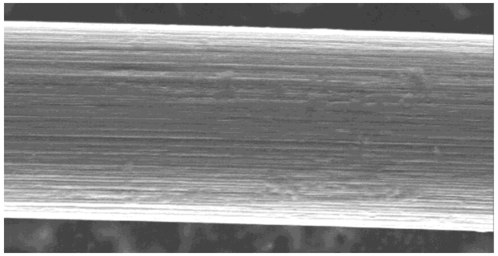
After ACP biodegradation studies the bacterial colonisation was amplified

[12] I. Tapsoba, S. Bourhis, T. Feng, M. Pontié, **Electroanalysis** 2009, 21, 10, 1167-

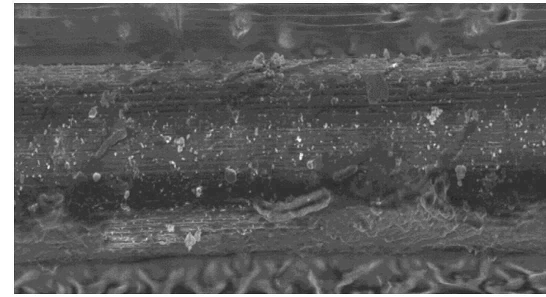
ANTIBIOFOULING STRATEGY IN 3 STEPS



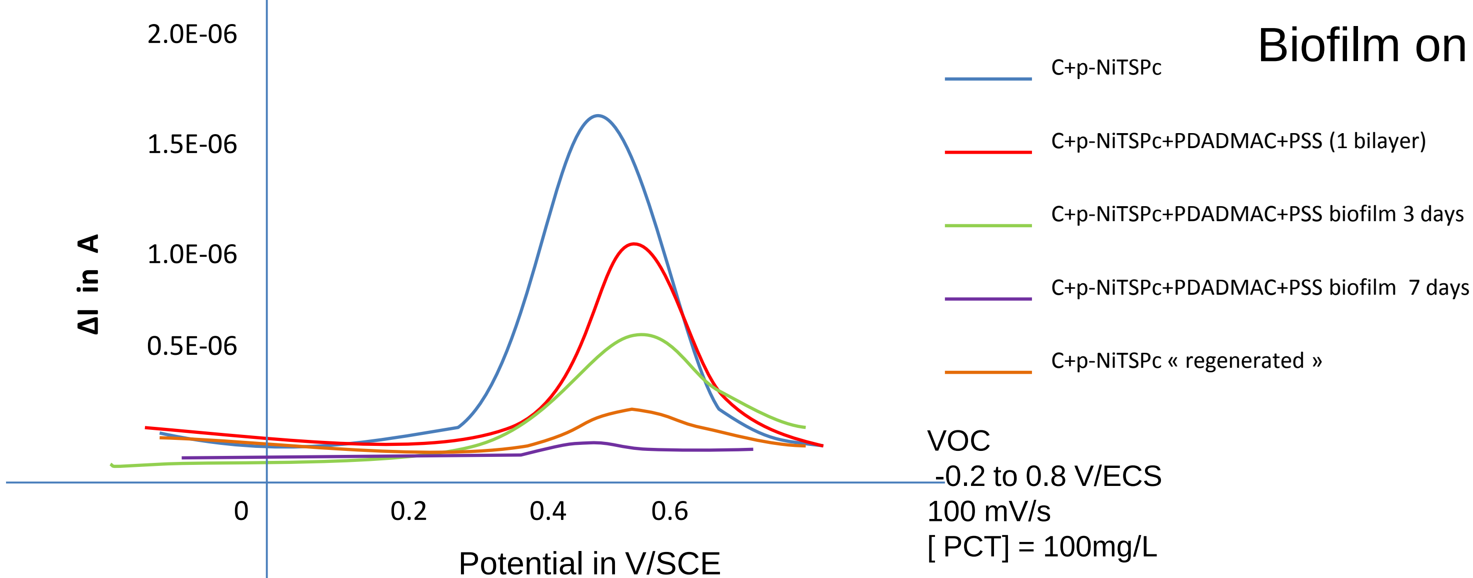
[13] S. Ben Rejeb, J. Legrand, M. Pontié, **Sep. Purif. Technology, 2012**



Pristine sensor

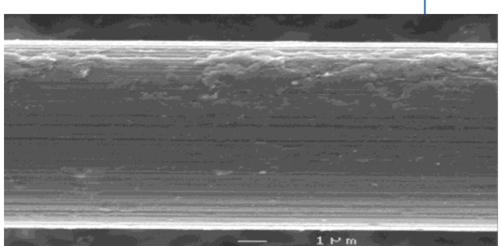


Biofilm on sensor



VOC
-0.2 to 0.8 V/ECS
100 mV/s
[PCT] = 100mg/L

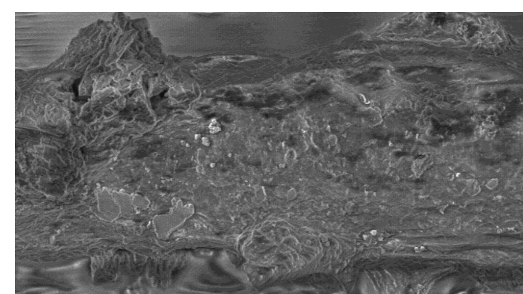
Regenerated sensor



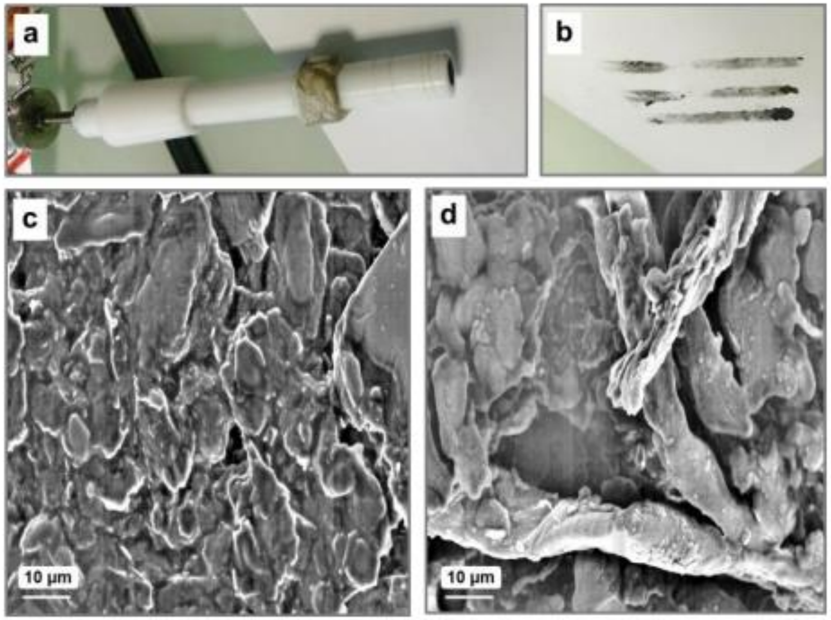
Sensor with 1 bilayer

VERY BAD REGENERATION

RESEARCH in development by testing multi-bilayers…



An other antibiofouling strategy : Carbon paste electrode !



Sensitive
« outerlayer » renewal
(3 lines of 3.5 cm) in 3
seconds !

We have a « stock » of 30 electrodes

LE STUDIUM CONFERENCES
ORLÉANS | 2018

Acknowledgements

ICMN team, Orléans

and PIERRE-YVES PONTALIER,
LCA Toulouse

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WATER CELL, CAPACITES
GEIHP Angers

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