

The logo for intersol 2013 features the word "intersol" in orange and "2013" in blue, with a stylized sun or sphere graphic between the two words.

Congrès-Exposition International sur les Sols, les Sédiments et l'Eau  
International Conference-Exhibition on Soils, Sediments and Water



# **GRAFTING OF CYSTEINE ON GEOTEXTILES TO TRAP HEAVY METALS FROM POLLUTED SOLUTIONS**

*GREFFAGE DE CYSTÉINE SUR GÉOTEXTILES AFIN DE CAPTER LES MÉTAUX LOURDS PRÉSENTS DANS DES SOLUTIONS POLLUÉES*

**28/03/2013**

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# Context

Current issue: heavy metals in sediments  
DEPOLTEX Project

## Biomolecules Grafting on geotextile

Functionalization process  
Immobilization of biomolecules

## Biomolecules of interest

Interesting biomolecules  
Cysteine

## Experimental results

Optimization of the grafting of cysteine  
Characterization of the grafting  
Heavy metals trapping tests

## Current issue

- Accumulation of sediments in harbor, canals, rivers, streams
  - Dunkerque: 3 millions m<sup>3</sup> / year dredged marine sediments
  - Sediments without contamination: immersed in seas
  - Contaminated sediments: storage center (expensive)
- 
- Sustainable development: valorization of sediments from harbor (treatment to remove heavy metals)
  - Recyclability and valorization of heavy metals trapped in the process



## Depoltex project

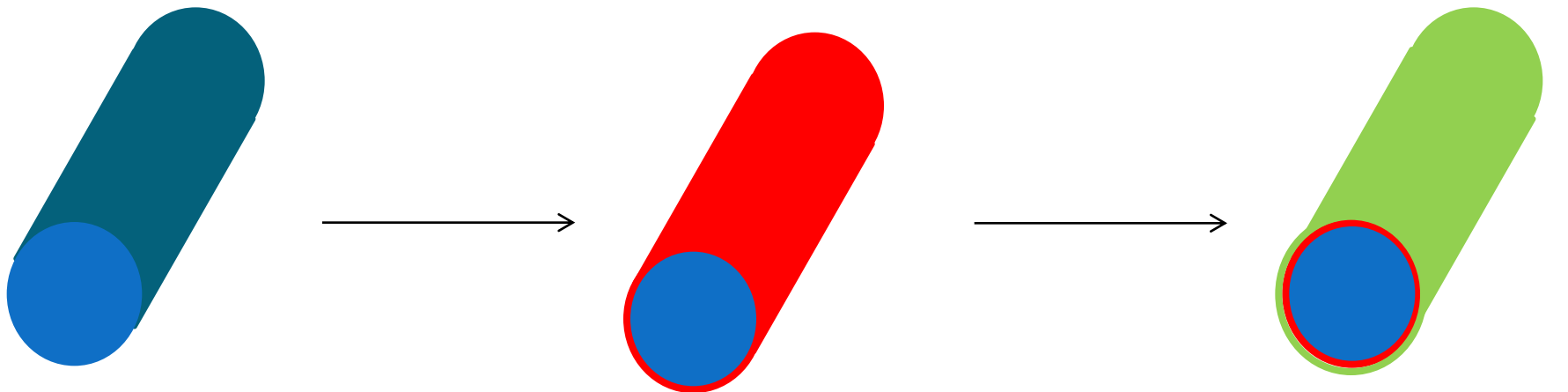
# ***Design for Environment and development of Depolluting Geotextiles for the Treatment of dredged sediments***

## Purpose

**Elaboration of functionalized geotextiles by physical methods to trap  
heavy metals in dredged sediments**

## Functionalization process

- Covalent grafting of molecules on the textile
- Functionalization → acidic functions at the surface
- Immobilization of biomolecule



Virgin PP fiber

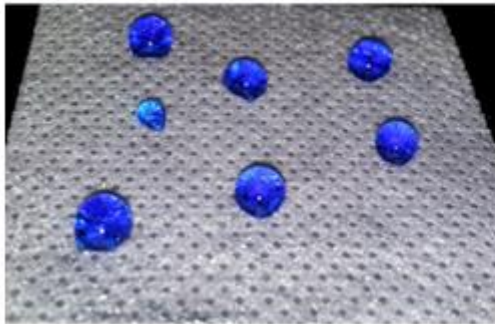
Acidic groups on PP fiber

Biomolecules on PP fiber

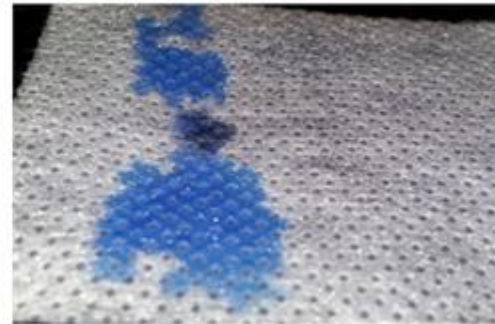
## Activation of the textile by cold plasma

- Geotextile (use in drainage and filtration) : Polypropylene nonwoven (INTN50, PGI)
- **Issue** : polypropylene (PP) → hydrophobic
- ✓ Cold plasma process (radio frequency), argon flow → hydrophilic textile

Before Plasma

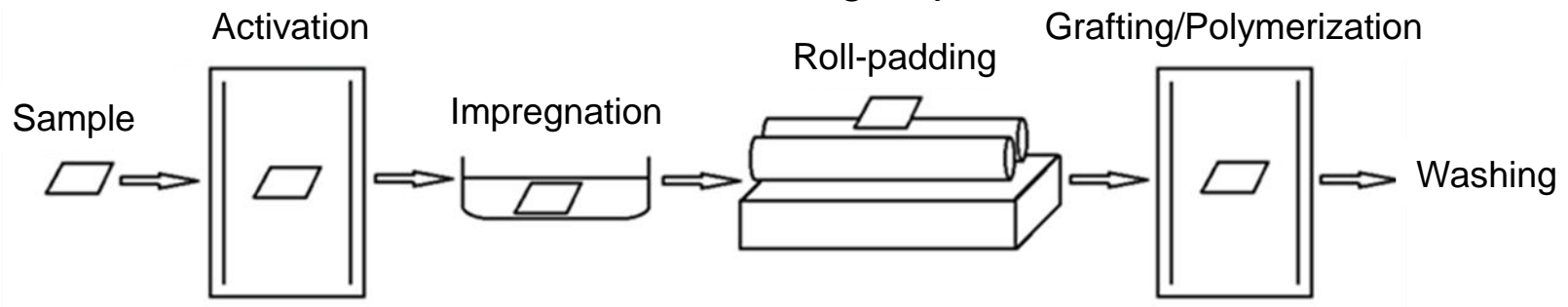


After Plasma

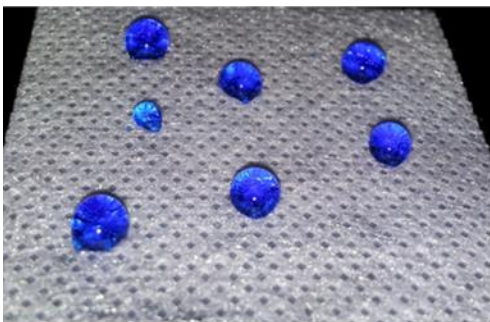


## Functionalization of the geotextile

- Geotextile (use in drainage and filtration) : Polypropylene nonwoven (INTN50, PGI)
- ~~➤ Direct grafting of biomolecules~~ Not enough reactive functions at the textile surface
- ✓ Grafting of acrylic and polyacrylic acid<sup>1</sup> → acrylic acid small molecule, easy to graft  
→ acidic groups on the textile



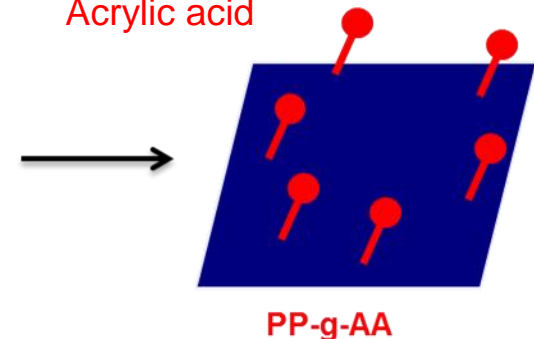
Before Plasma



After Plasma



Acrylic acid



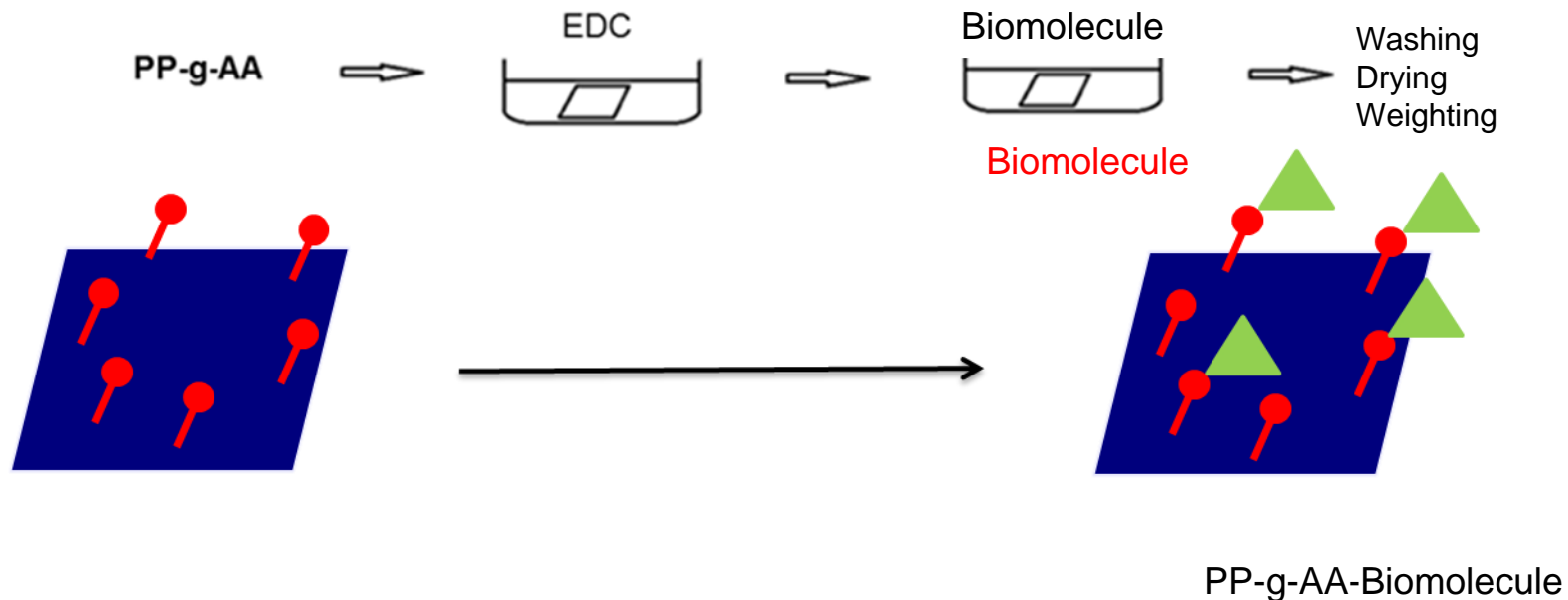
PP-g-AA

Optimized<sup>1</sup>

<sup>1</sup> *Biomedical Materials*, **2012**, 7 (3), 1-13, art. no.035001

## Immobilization of the biomolecules

- Geotextile (use in drainage and filtration) : Polypropylene nonwoven (INTN50, PGI)
- ✓ Chemical grafting / coupling reagent : carbodiimide



<sup>2</sup> *Reactive and Functional Polymers*, **2013**, 73 (1), 53-59



## Biomolecules of interest

| Biomolecules     | Structure                              | Trapped metals     | References |
|------------------|--|--------------------|------------|
| Glutathione      | $\gamma$ -Glu-Cys-Gly                  | Hg, Pb, Cd         | 3, 4       |
| Phytochelatins   | $(\gamma\text{-Glu-Cys})_n\text{-Gly}$ | Cd, Pb, As, Cu     | 5          |
| Metallothioneins | Cys-x-Cys<br>Cys-x-x-Cys<br>Cys-Cys    | Pb, Hg, Cd, Cu, Zn | 6, 7, 8    |

Glu : Glutamic acid

Cys : Cysteine

Gly : Glycine

X : Amino acid

All these natural chelating biomolecules  
have something in common...

<sup>3</sup> *the FEBS Journal*, **2010**, 277 (24), 5086-5096

<sup>4</sup> *EMBO reports*, **2005**, 6 (6), 497-501

<sup>5</sup> *Gene*, **1996**, 179 (1), 21-30

<sup>6</sup> *The Journal of Biological Chemistry*, **2001**, 276 (35), 32835-32843

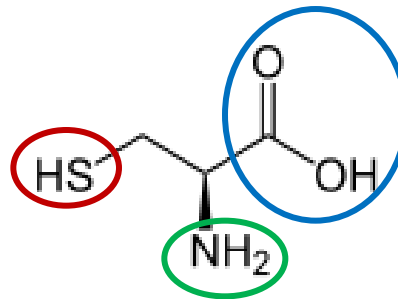
<sup>7</sup> *Proceedings of the National Academy of Sciences (USA)*, 1997, 95, 2233-2237

<sup>8</sup> *Annual Review of Pharmacology and Toxicology*, **1999**, 39, 267-294

## Cysteine

... Cysteine

- One of the most important amino acid for life organisms



- 3 important functions: **thiol**, **amine**, **carboxylic acid**
- **Amino group** → used in the immobilization of the biomolecule on PP-g-AA

## Optimization of the grafting of cysteine

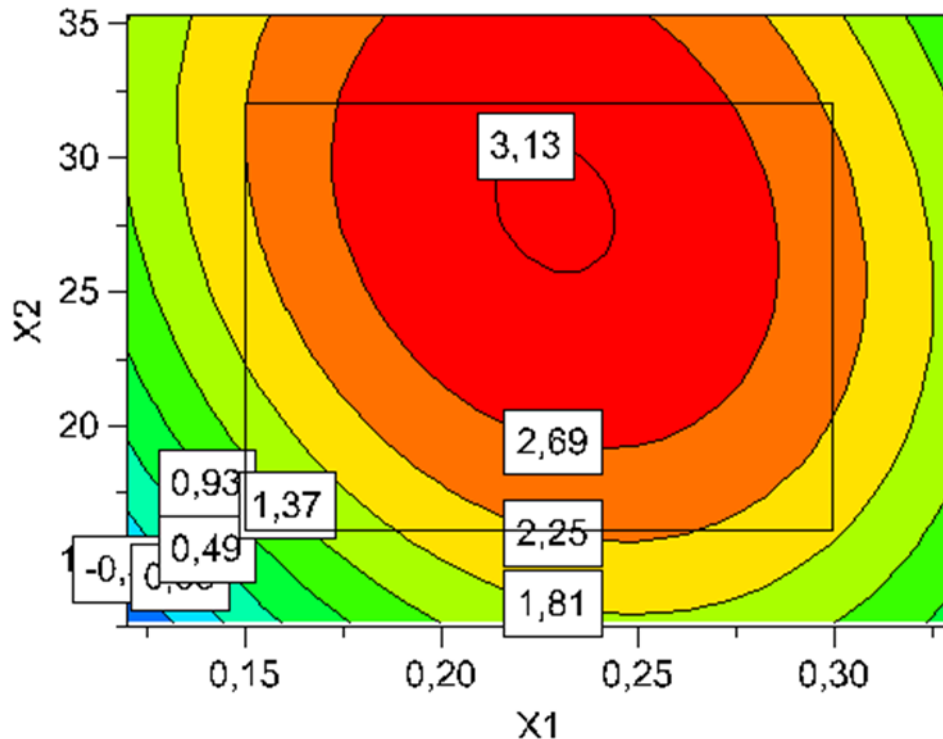
Central composite design

- Parameters

| Coded variables | Parameters                           | Levels    |      |       |      |           |
|-----------------|--------------------------------------|-----------|------|-------|------|-----------|
|                 |                                      | $-\alpha$ | -1   | 0     | +1   | $+\alpha$ |
| $X_1$           | $U_1$ cysteine concentration (mol/L) | 0.12      | 0.15 | 0.225 | 0.30 | 0.33      |
| $X_2$           | $U_2$ immersion time (h)             | 12h40     | 16h  | 24h   | 32h  | 35h20     |

- Response : grafting rate

## Optimization of the grafting of cysteine



Contour plot → evolution of the cysteine grafting as function of cysteine concentration ( $X_1$ ) and immersion time ( $X_2$ )

Optimum conditions:

$U_1 = 0.229$  mol/L cysteine

$U_2 = 28$  hours (immersion time)

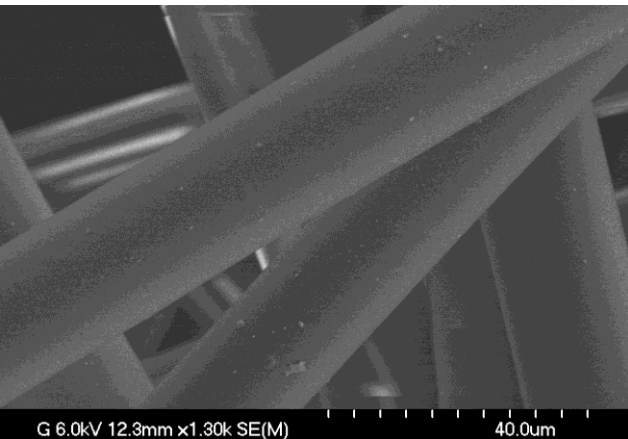
According to the model:  
Grafting rate = 3.16%

Experimentally :  $3.2 \pm 0.5$  %

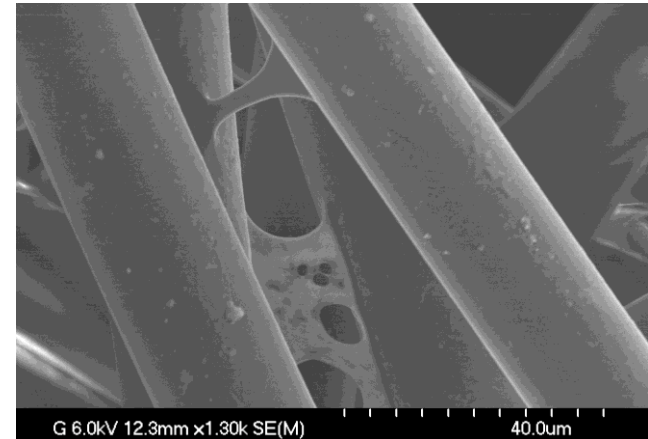
- Recent studies: increase of the temperature in order to decrease the immersion time (immersion for 1 hour at 50°C leads to the same results)

## Surface characterization

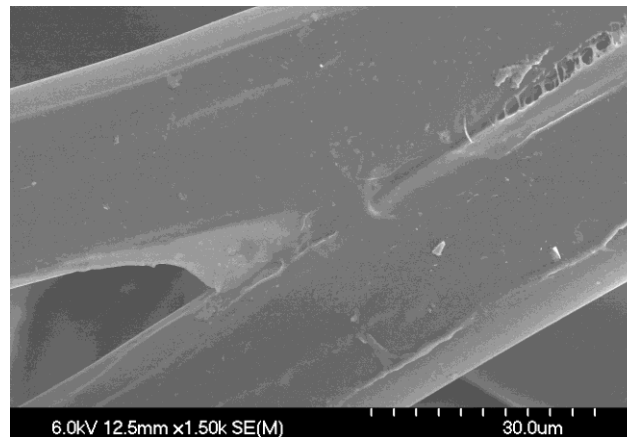
### 1) Scanning Electron Microscopy (secondary electrons)



Virgin PP

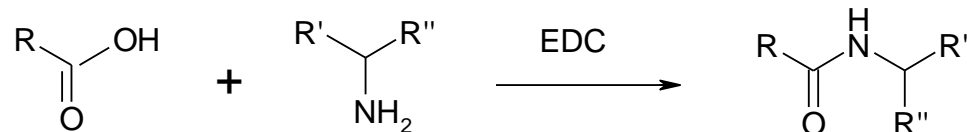


PP-g-AA

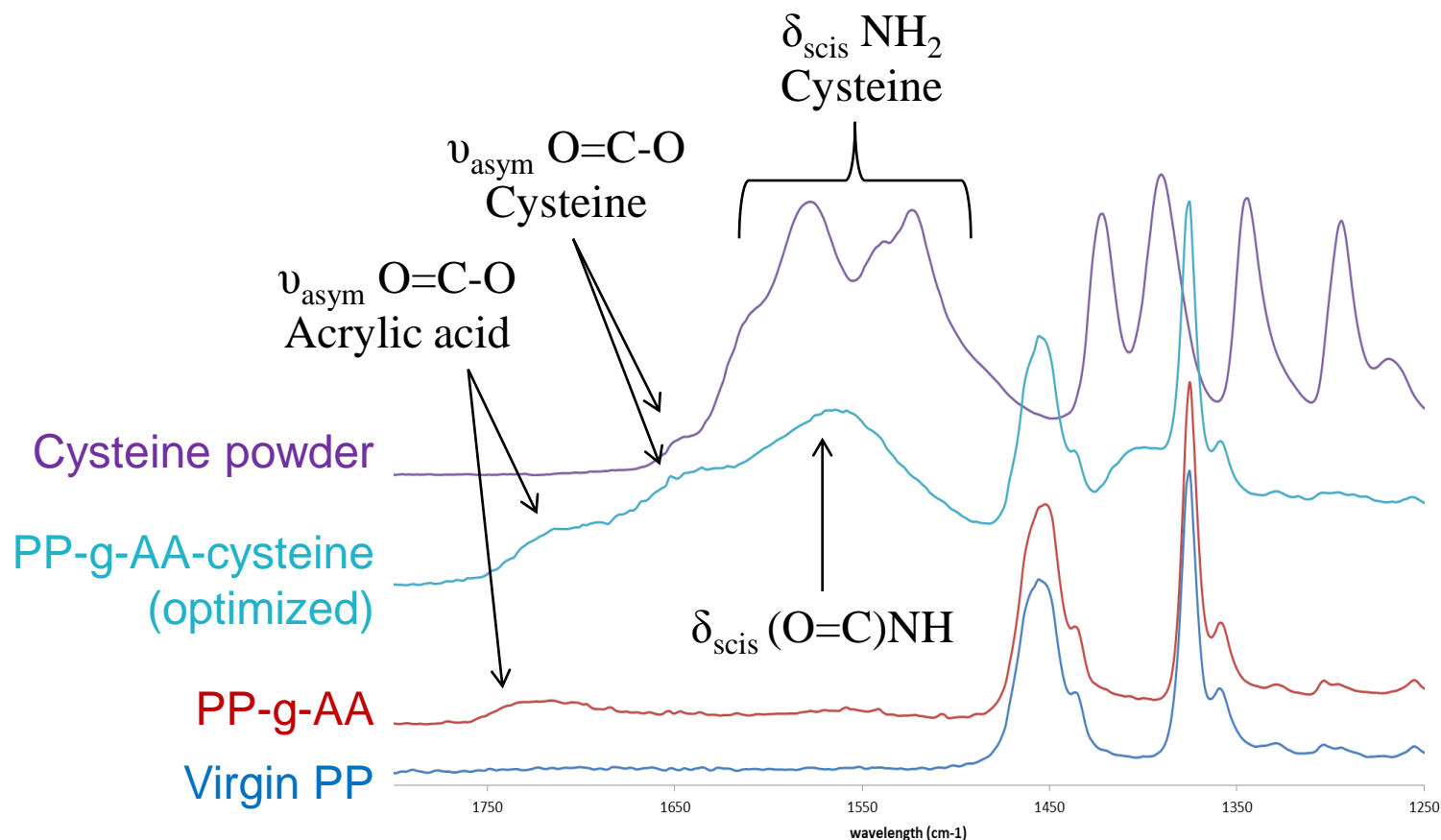


PP-g-AA-Cysteine  
(Optimized)

## Surface characterization



- 1) Scanning Electron Microscopy (secondary electrons)
- 2) Fourier Transform Infrared Spectroscopy / Attenuated Total Reflectance



Formation of  
an amide  
group

→ Covalent  
grafting

## Surface characterization

- 1) Scanning Electron Microscopy (secondary electrons)
- 2) Fourier Transform Infrared Spectroscopy / Attenuated Total Reflectance
- 3) X-ray Photoelectron Spectroscopy

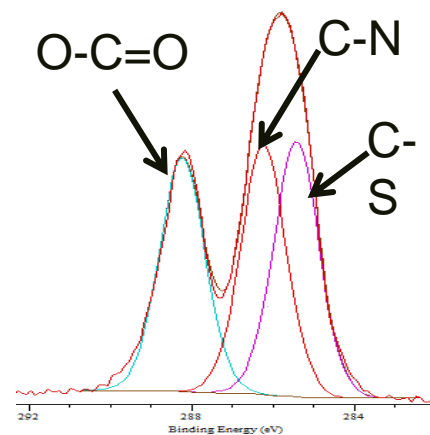
| Samples          | C1s  | O1s  | N1s | S2p | [O1s]/[C1s] % | [N1s]/[C1s] % | [S2p]/[C1s] % |
|------------------|------|------|-----|-----|---------------|---------------|---------------|
| PP               | 97.4 | 2.6  | 0   | 0   | 2.7           | 0             | 0             |
| PP-g-AA          | 82.1 | 17.9 | 0   | 0   | 22            | 0             | 0             |
| PP-g-AA-cysteine | 68.9 | 25.1 | 3.7 | 2.3 | 36            | 5.4           | 3.3           |

% C-C : 54.3 ← PP, AA

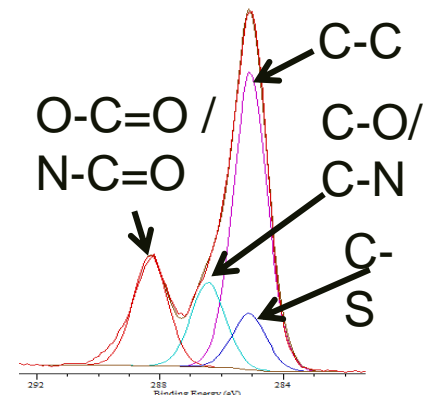
% C-O / C-N : 15.4

% O-C=O / N-C=O: 20.1 } AA et cysteine

% C-S : 10.28 } Cysteine



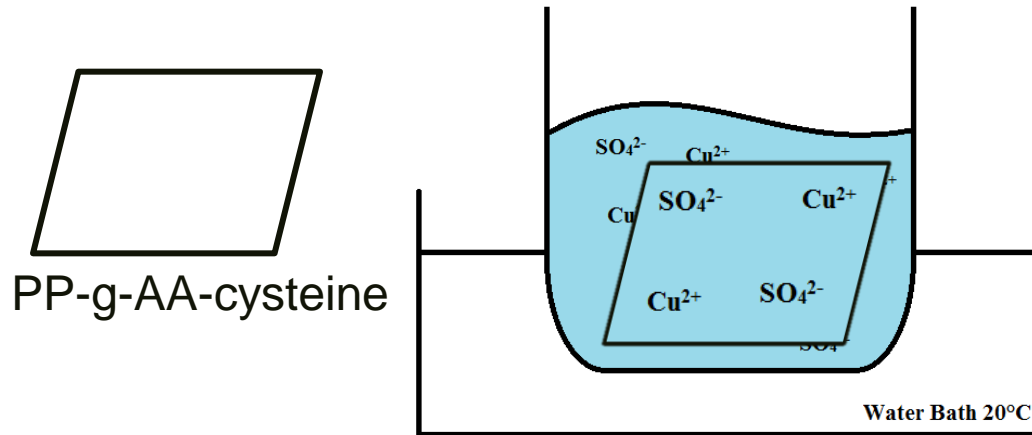
C1s Cysteine



C1s PP-g-AA-Cysteine

## Heavy metals trapping tests

Tests with artificially polluted solutions:  $\text{CuSO}_4$ ,  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Cr}(\text{NO}_3)_3$



PP-g-AA-cysteine +  $\text{Cu}^{2+}$

Washing with ultrapure water

└─ Digestion of the surface

└─ Atomic absorption

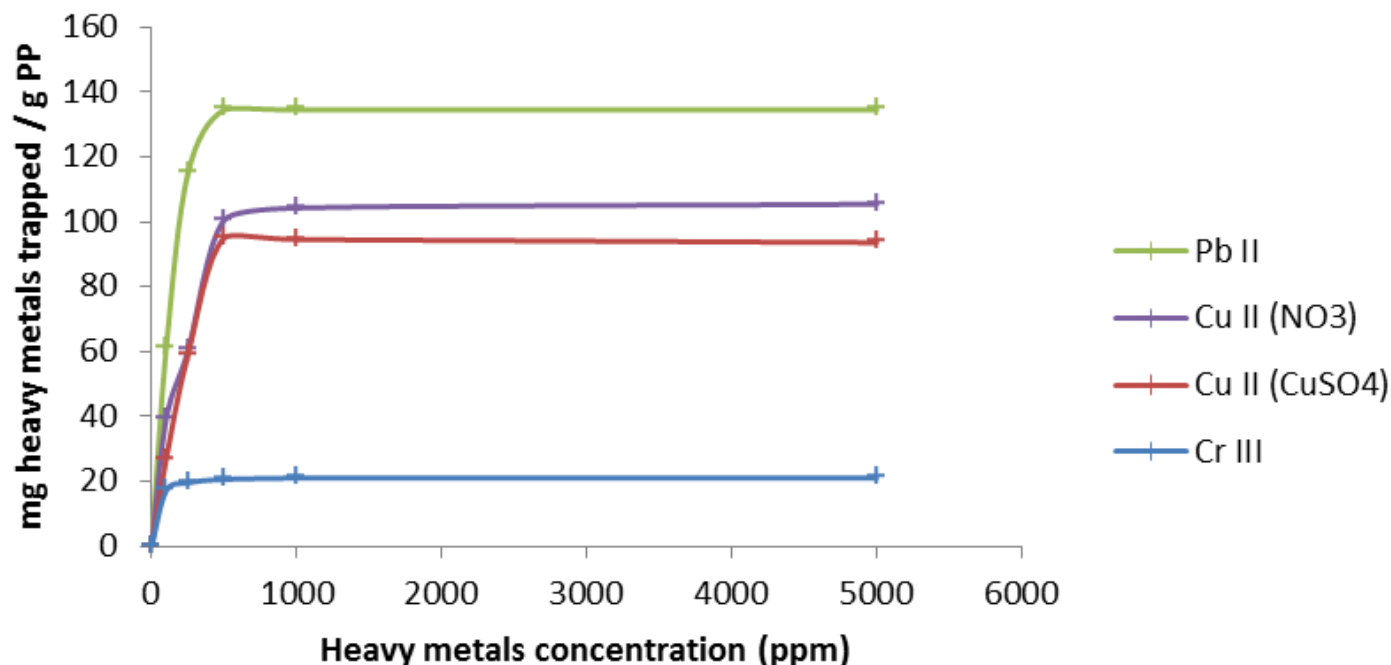




## Heavy metals trapping tests

Evolution of the concentration

saturation: ~500 ppm heavy metals in 100 mL (pH = 4.5)



PP-g-AA-cysteine

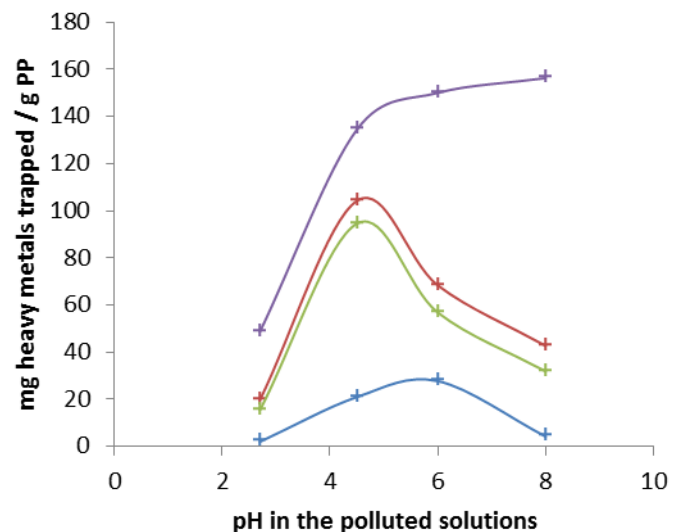
$\text{CuSO}_4 \rightarrow 95 \text{ mg/g PP} \rightarrow 1.5 \text{ mmol/g PP}$   
 $\text{Cu(NO}_3)_2 \rightarrow 104 \text{ mg/g PP} \rightarrow 1.6 \text{ mmol/g PP}$   
 $\text{Pb(NO}_3)_2 \rightarrow 135 \text{ mg/g PP} \rightarrow 0.7 \text{ mmol/g PP}$   
 $\text{Cr(NO}_3)_3 \rightarrow 21 \text{ mg/g PP} \rightarrow 0.4 \text{ mmol/g PP}$

PP-g-AA

$17 \text{ mg/g PP}$   
 $18 \text{ mg/g PP}$   
 $48 \text{ mg/g PP}$   
 $11 \text{ mg/g PP}$

## Heavy metals trapping tests

### Effect of the pH



### Optimal trapping

pH optimum (copper) = 4.8

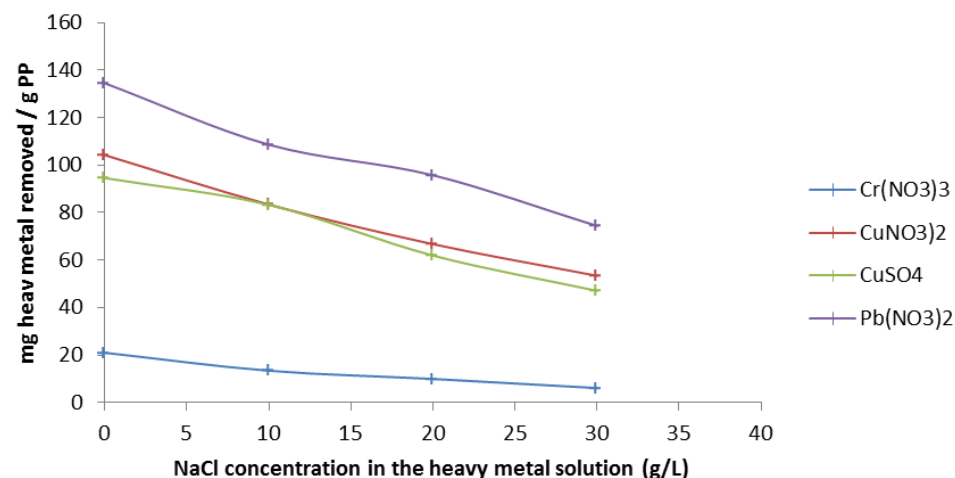
pH optimum (chromium) = 6

pH optimum (lead) > 8 ?

### Effect of the ionic strength

Trapping of heavy metals decreases

| mg/g PP                           | Soft water | Sea water |
|-----------------------------------|------------|-----------|
| CuSO <sub>4</sub>                 | 95         | 47        |
| Cu(NO <sub>3</sub> ) <sub>2</sub> | 104        | 53        |
| Pb(NO <sub>3</sub> ) <sub>2</sub> | 134        | 74        |
| Cr(NO <sub>3</sub> ) <sub>3</sub> | 21         | 6         |



# Conclusions and Outlooks

- ✓ Cysteine successfully grafted (SEM, FT-IR, XPS)
  - ✓ Trapping of heavy metals from artificially polluted solutions
  - ✓ Optimum pH for the trapping according to the metal: 4.8 for copper, 6 for chromium.
  - ✓ Issue: presence of NaCl decreases the trapping
- 
- Immobilization of other biomolecules (tyrosine)
  - Trapping of heavy metals from sediments and leachates
  - Use of other methods (for the grafting): atmospheric plasma, excimer LASER

The logo for intersol 2013 features the word "intersol" in red and blue, with a stylized yellow and orange sun-like graphic in the "o", followed by "2013" in blue. The background is a green and yellow abstract design.

**intersol 2013**

Congrès-Exposition International sur les Sols, les Sédiments et l'Eau  
International Conference-Exhibition on Soils, Sediments and Water

The logo for up tex features the word "up" in blue, with a blue underline, followed by "tex" in grey.

(uptex

# THANK YOU FOR YOUR ATTENTION

The logo for UMET features the word "UMET" in blue, with a blue underline, followed by "Unité Matériaux Et Transformations" in smaller blue text.

**UMET**  
Unité Matériaux Et Transformations

The logo for Chimie Lille features the word "Chimie" in grey, a red fleur-de-lis, and the word "Lille" in grey, with "ÉCOLE NATIONALE" and "SUPÉRIEURE DE CHIMIE" in smaller grey text below.

*Chimie*  *Lille*  
ÉCOLE NATIONALE SUPÉRIEURE DE CHIMIE

The logo for Université Lille1 features a blue globe icon, followed by "Université Lille1" and "Sciences et Technologies" in black text.

 **Université  
Lille1**  
Sciences et Technologies

# THANKS TO THE PARTNERS OF THE DEPOLTEX PROJECT

The logo for oseo features the word "oseo" in brown, with a red dot above the "o" and a yellow swoosh below the "o".

**oseo**

The logo for the Région Nord-Pas de Calais features a blue and yellow stylized icon, followed by "RÉGION Nord-Pas de Calais" in black text.

 **RÉGION  
Nord-Pas de Calais**

The logo for l'Europe s'engage en Nord-Pas-de-Calais features a blue circle with yellow stars, followed by "l'Europe s'engage en Nord-Pas-de-Calais" and "avec le FEDER" in black text.

 **l'Europe  
s'engage  
en  
Nord-Pas-de-Calais**  
avec le **FEDER**