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

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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

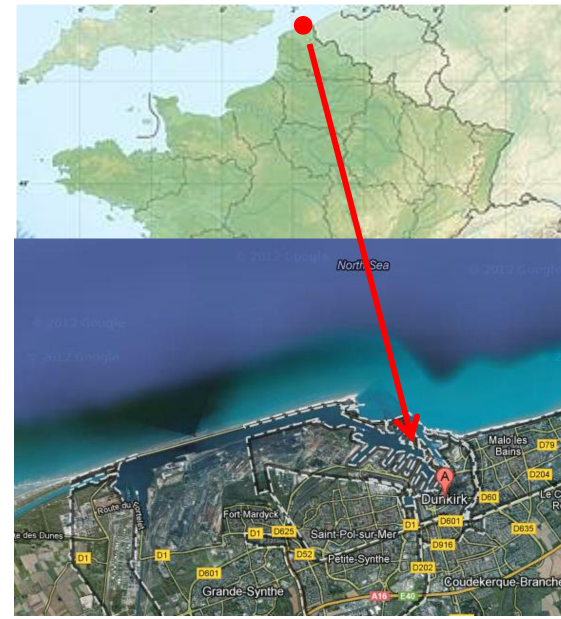
Interesting biomolecules
Cysteine

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^3 / 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

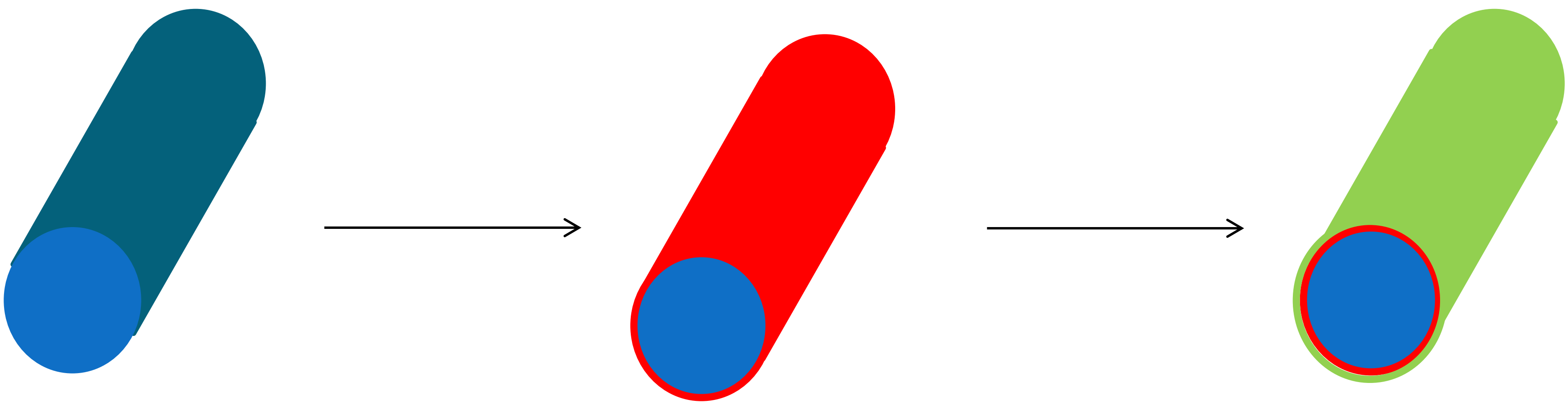
Design for Environment and development of Depolluting Geotextiles for the Treatment of dredged sediments

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

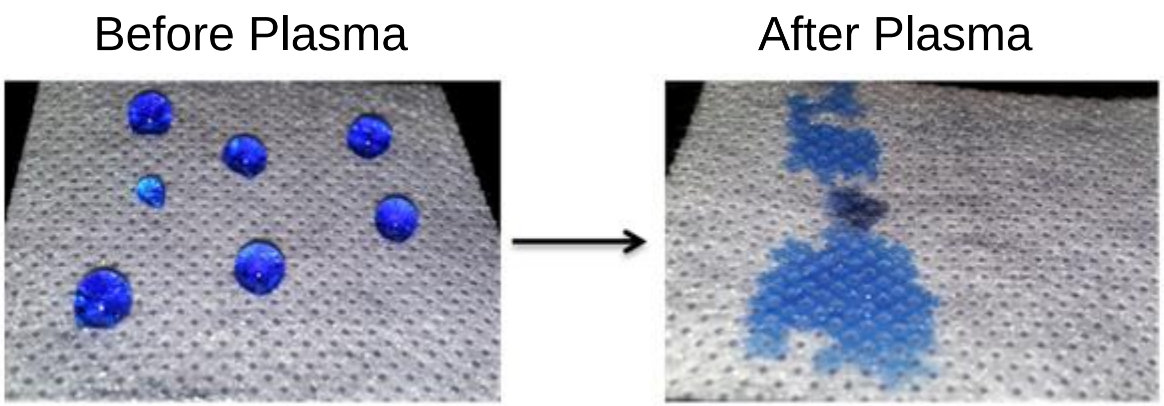


Virgin PP fiber | Acidic groups on PP fiber | Biomolecules on PP fiber

Activation of the textile by cold plasma

- Geotextile (use in drainage and filtration) : Polypropylene nonwoven (INTN50, PGI)
- **Issue** : polypropylene (PP) → hydrophobic

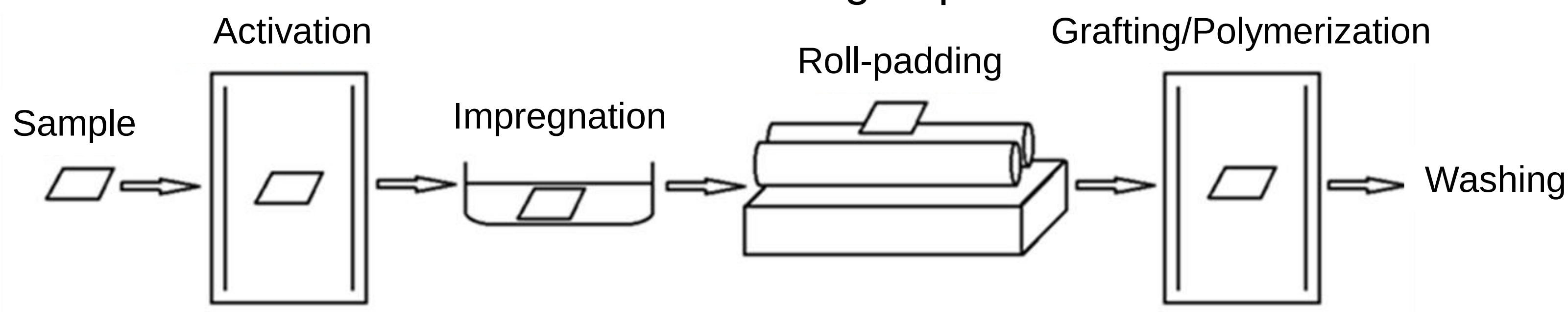
✓ Cold plasma process (radio frequency), argon flow → hydrophilic textile



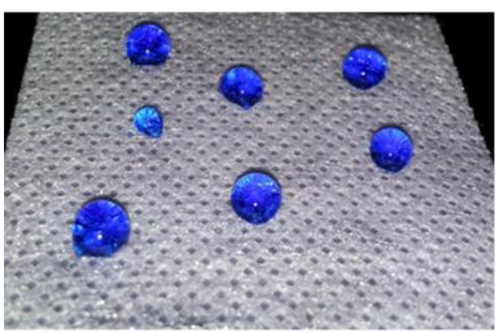
Functionalization of the geotextile

- Geotextile (use in drainage and filtration) : Polypropylene nonwoven (INTN50, PGI)
- ~~Direct grafting of biomolecules~~ Not enough reactive functions at the textile surface

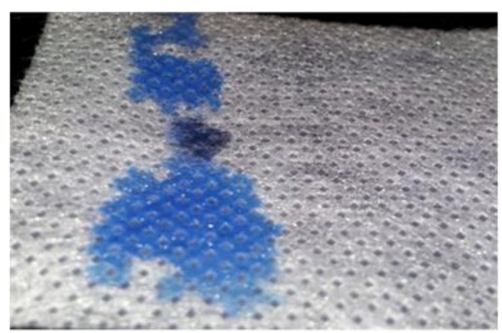
✓ Grafting of acrylic and polyacrylic acid[1] → acrylic acid small molecule, easy to graft
→ acidic groups on the textile

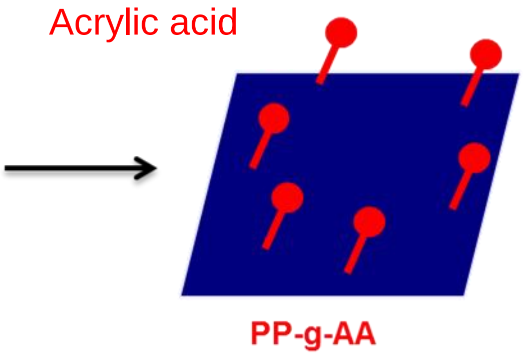


Before Plasma



After Plasma





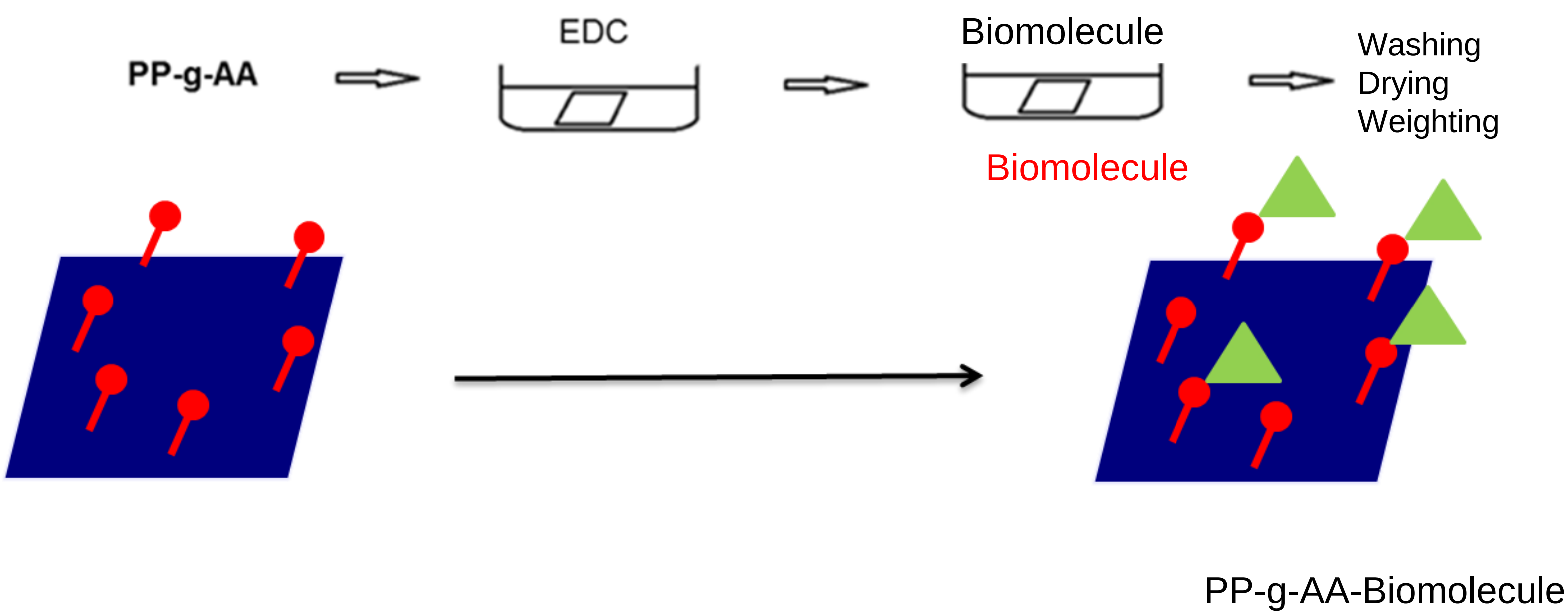
[1] *Biomedical Materials*, **2012**, 7 (3), 1-13, art. no.035001

Optimized[1]

Immobilization of the biomolecules

➢ Geotextile (use in drainage and filtration) : Polypropylene nonwoven (INTN50, PGI)

✓ Chemical grafting / coupling reagent : carbodiimide



[2] *Reactive and Functional Polymers*, **2013**, 73 (1), 53-59

Biomolecules of interest

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

Glu : Glutamic acid
Cys : Cysteine
Gly : Glycine
X : Amino acid

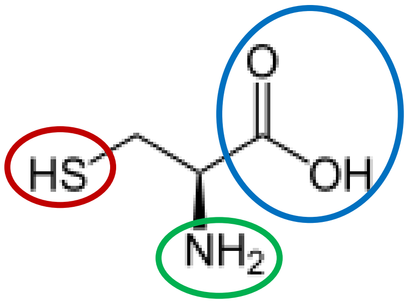
All these natural chelating biomolecules have something in common…

[3] *the FEBS Journal*, **2010**, 277 (24), 5086-5096
[4] *EMBO reports*, **2005**, 6 (6), 497-501
[5] *Gene*, **1996**, 179 (1), 21-30
[6] *The Journal of Biological Chemistry*, **2001**, 276 (35), 32835-32843
[7] *Proceedings of the National Academy of Sciences (USA)*, 1997, 95, 2233-2237
[8] *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

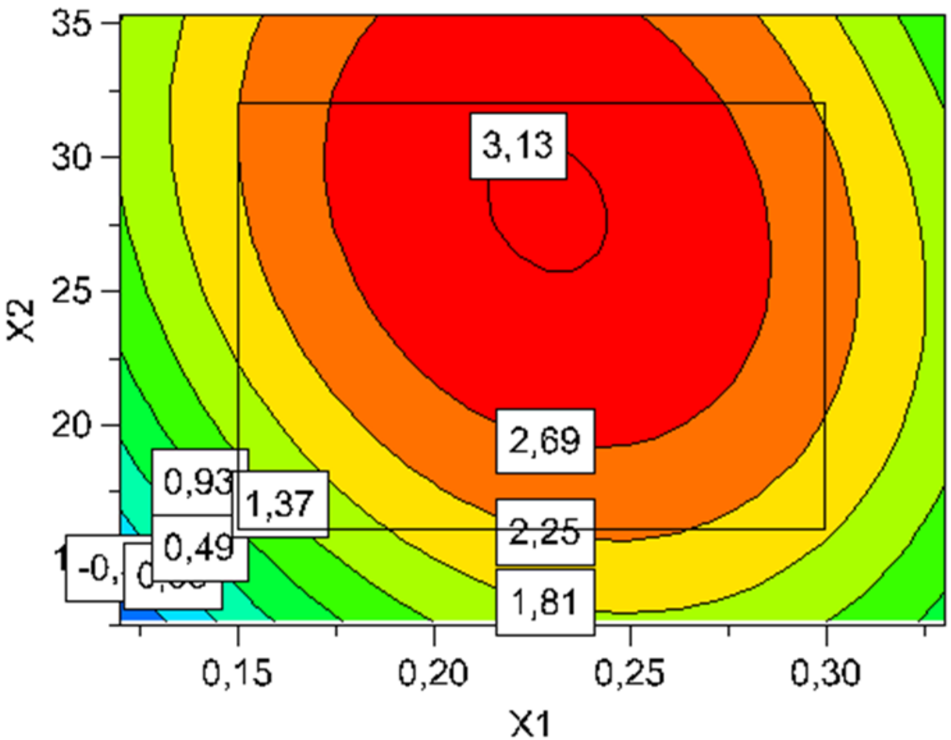
Central composite design

- Parameters

Coded variables	Parameters	Levels				
		-α	-1	0	+1	+α
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)

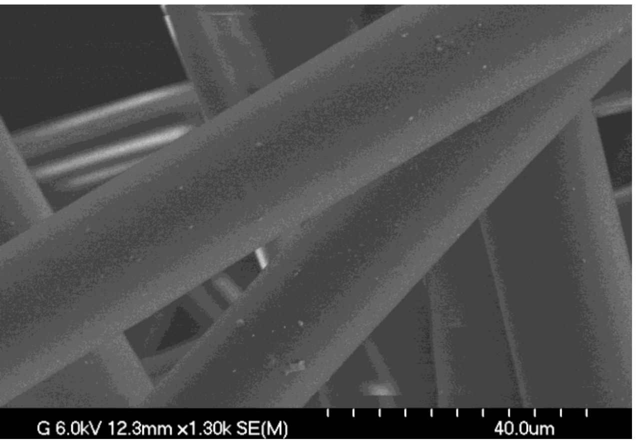
According to the model:
Grafting rate = 3.16%

Experimentally :3.2 ± 0.5 %

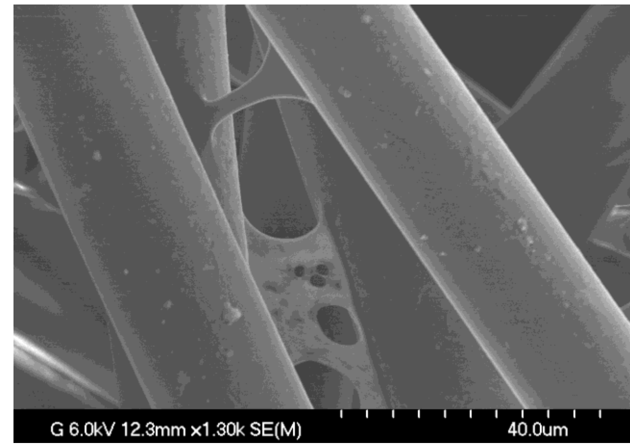
- Recent studies: increase of the temperature in order to decrease the immersion time (immersion for 1 hour at 50°C leads to the same results)

Surface characterization

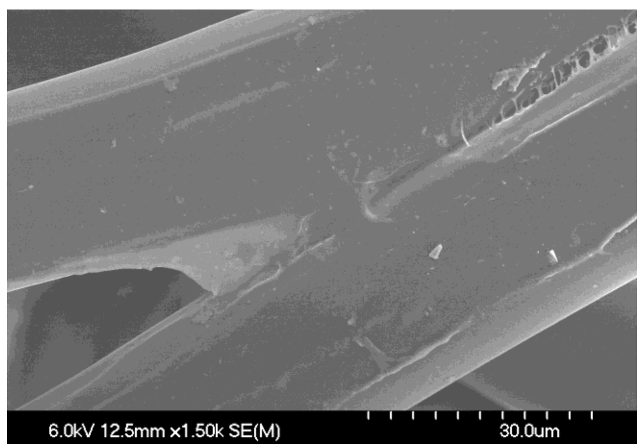
1) Scanning Electron Microscopy (secondary electrons)



Virgin PP

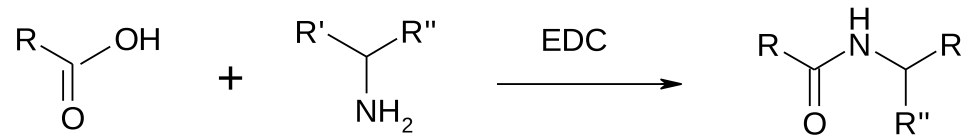


PP-g-AA

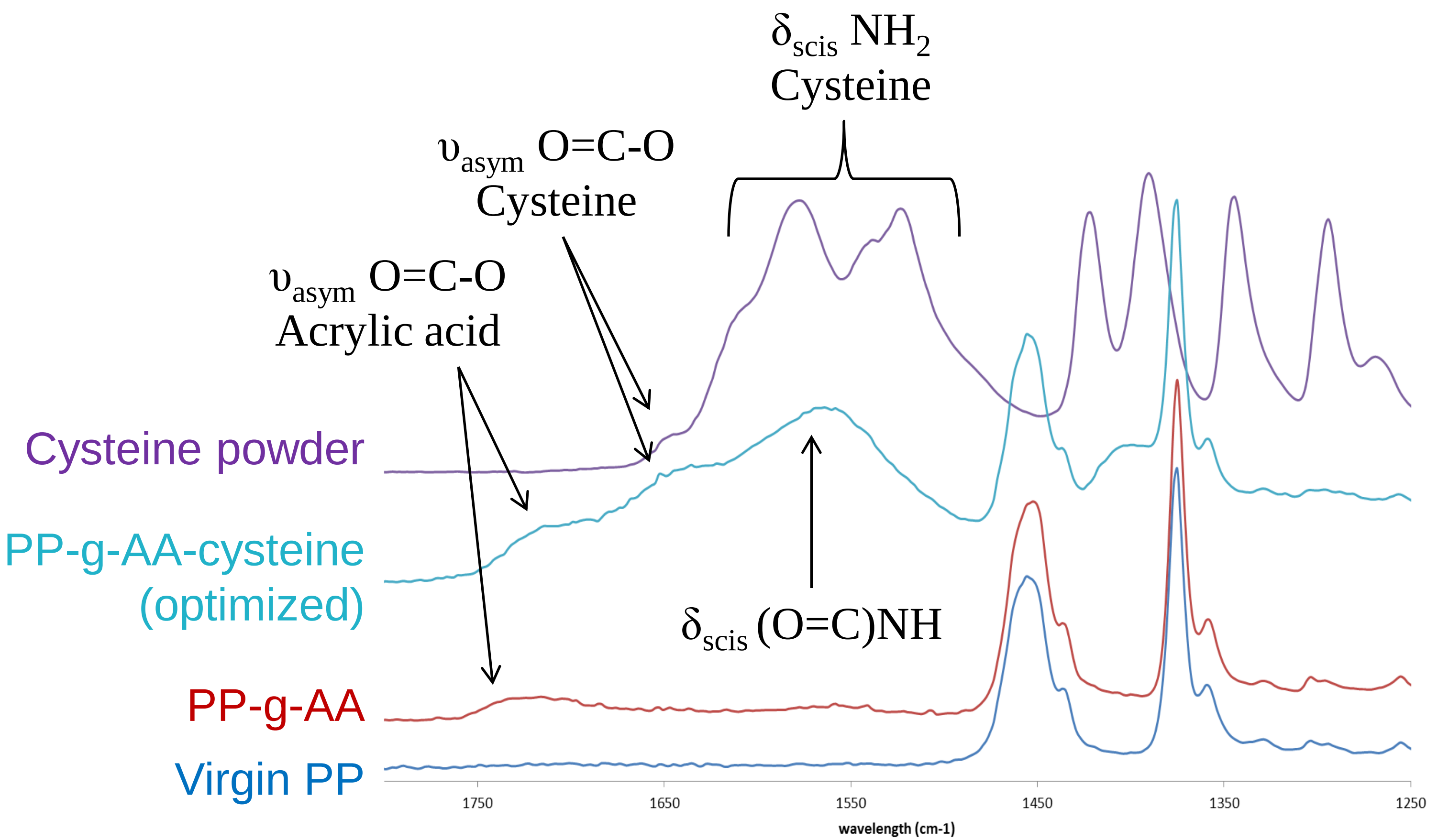


PP-g-AA-Cysteine
(Optimized)

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

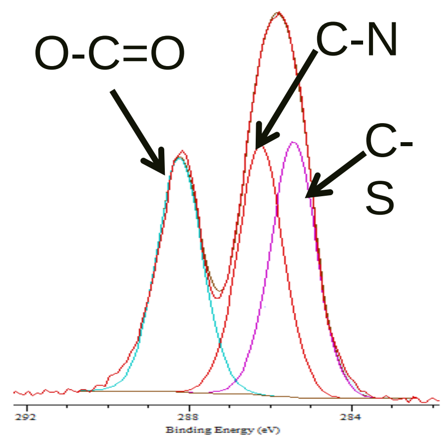
1) Scanning Electron Microscopy (secondary electrons)
2) Fourier Transform Infrared Spectroscopy / Attenuated Total Reflectance
3) X-ray Photoelectron Spectroscopy

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

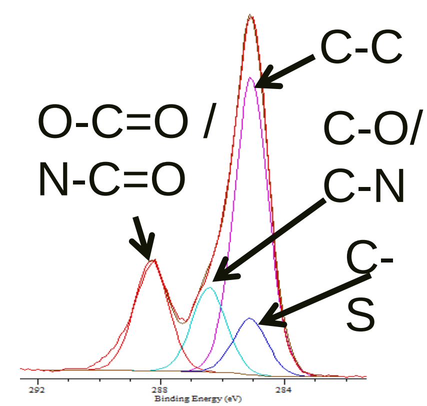
% C-C : 54.3 ← PP, AA

% C-O / C-N : 15.4
% O-C=O / N-C=O: 20.1
] AA et cysteine

% C-S : 10.28 } Cysteine



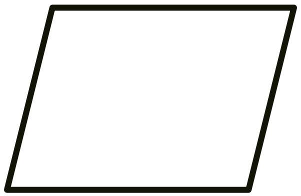
C1s Cysteine



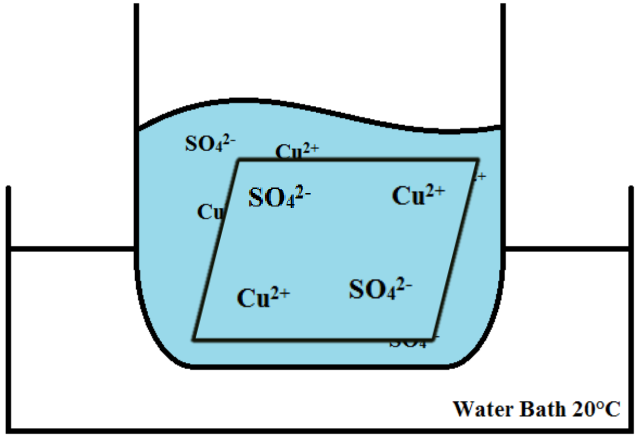
C1s PP-g-AA-Cysteine

Heavy metals trapping tests

Tests with artificially polluted solutions: $CuSO_4$, $Cu(NO_3)_2$, $Pb(NO_3)_2$, $Cr(NO_3)_3$



PP-g-AA-cysteine



PP-g-AA-cysteine + Cu^{2+}

Washing with ultrapure water

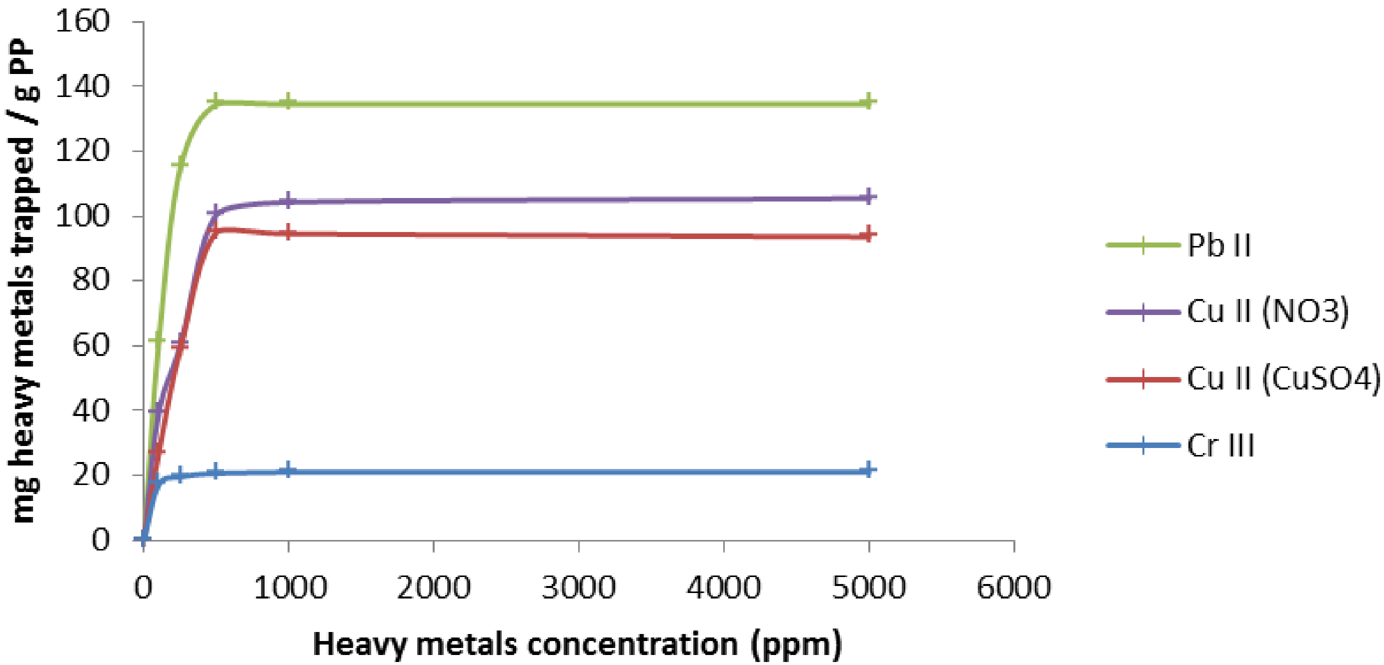
Digestion of the surface

Atomic absorption

Heavy metals trapping tests

Evolution of the concentration

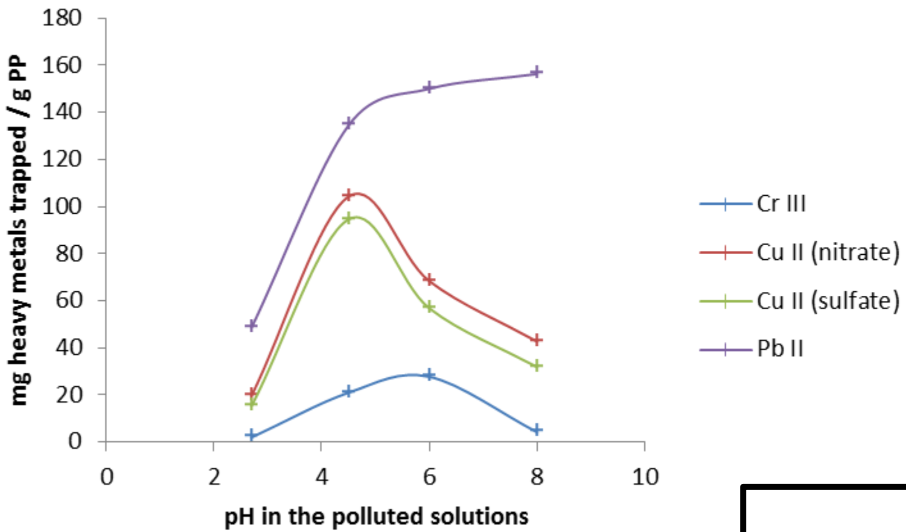
saturation: ~500 ppm heavy metals in 100 mL (pH = 4.5)



	PP-g-AA-cysteine				PP-g-AA
$CuSO_4$	→	95 mg/g PP	→	1.5 mmol/g PP	17 mg/g PP
$Cu(NO_3)_2$	→	104 mg/g PP	→	1.6 mmol/g PP	18 mg/g PP
$Pb(NO_3)_2$	→	135 mg/g PP	→	0.7 mmol/g PP	48 mg/g PP
$Cr(NO_3)_3$	→	21 mg/g PP	→	0.4 mmol/g PP	11 mg/g PP

Heavy metals trapping tests

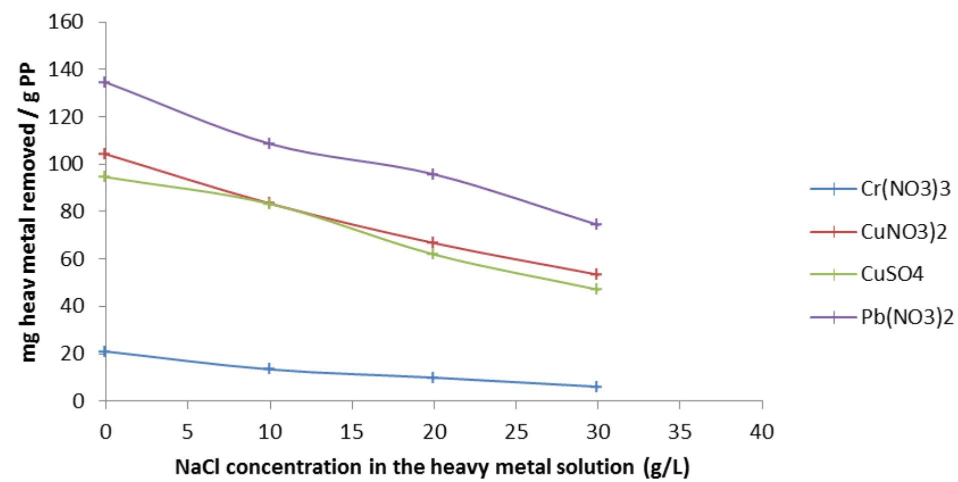
Effect of the pH



Effect of the ionic strength

Trapping of heavy metals decreases

mg/g PP	Soft water	Sea water
$CuSO_4$	95	47
$Cu(NO_3)_2$	104	53
$Pb(NO_3)_3$	134	74
$Cr(NO_3)_3$	21	6



Optimal trapping

pH optimum (copper) = 4.8

pH optimum (chromium) = 6

pH optimum (lead) > 8 ?

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

THANK YOU FOR YOUR ATTENTION

THANKS TO THE PARTNERS OF THE DEPOLTEX PROJECT