



**POLITECNICO**  
MILANO 1863

# *Polysaccharide-Based Materials*

*OSCM Lab – Laboratory of Organic Synthesis, Catalysis, and Materials*

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**The fact:** Today, standard procedures for chemical processes require inexpensive reagents, used under the mildest possible conditions, in order to achieve the desired products in high chemical yields and high atom economy by following the common rules of “Green Chemistry”.

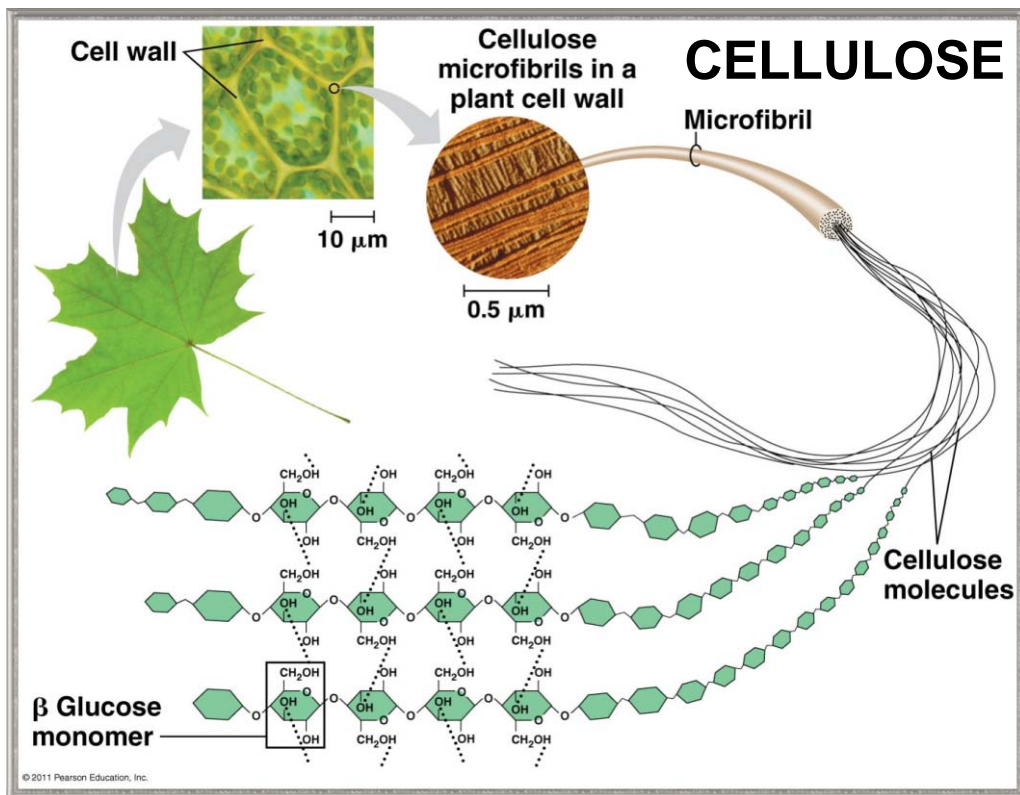
**Group’s aim:** To produce high added value organic products and materials for fine and basic chemistry and to meet growth, environmental and health expectations. This has to be obtained by a significant reduction of wastes and energy consumption with a consequent reduction in capital investment.

**How:** Our “motto” is understanding chemistry for making chemicals. Our approach consists in basic research, mechanism interpretation, and practical applications.

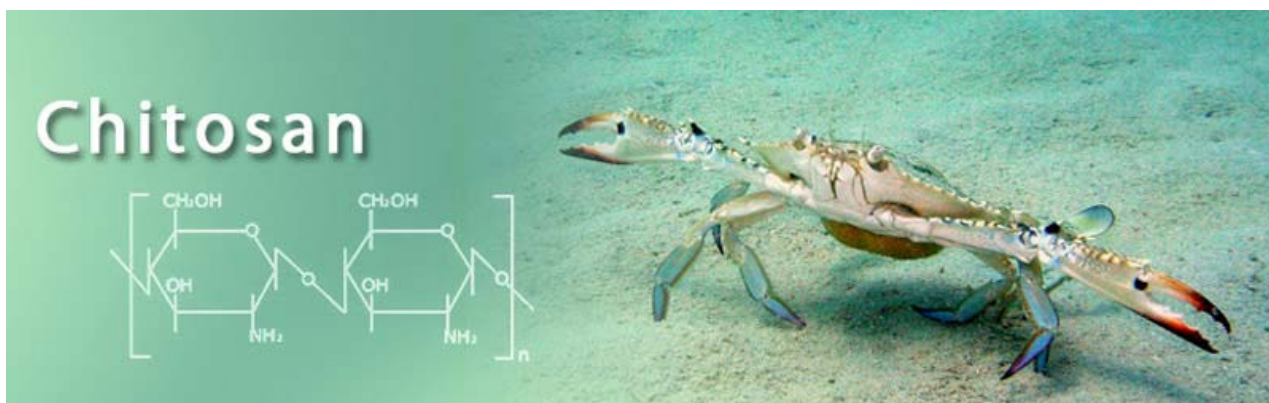
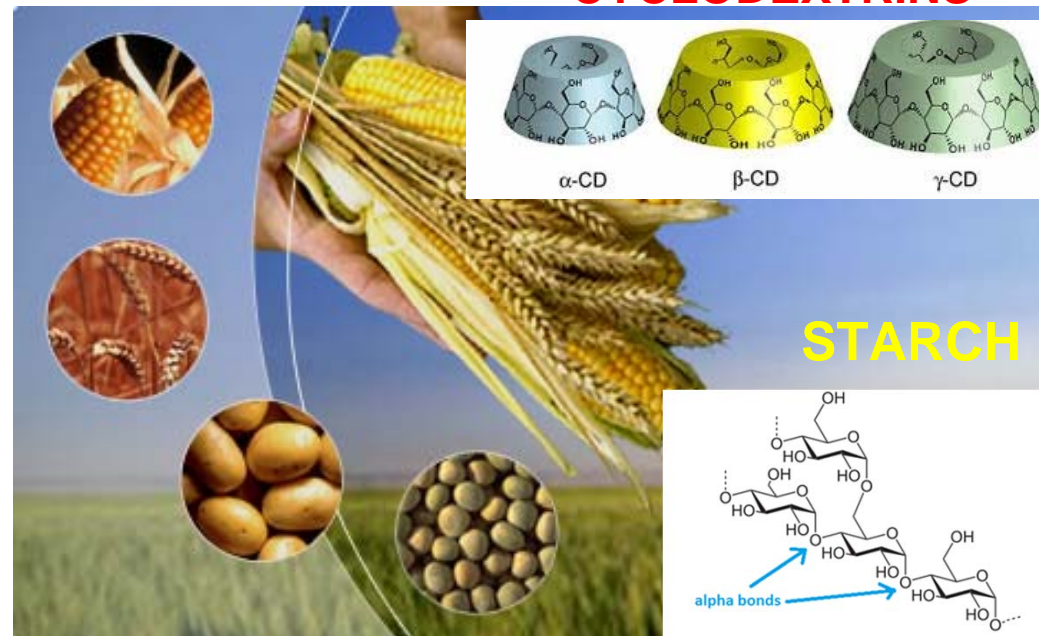
## Research fields:

- New catalytic systems for sustainable oxidations under mild conditions.
- Multicomponent reactions for advanced organic synthesis
- Organic vectors, gels, and materials for drug- and gene-delivery
- New sorbent materials for water, soil, and air decontamination
- Porous Coordination Polymers for novel applications

# Polysaccharide-based materials



## CYCLODEXTRINS



# Polysaccharide-based materials

## CYCLODEXTRINS



*Carbohydrate Polymers* **2017**, 165, 71-85.  
*ChemPlusChem* **2017**, 82, 848-858.  
*Biomacromolecules* **2016**, 17, 564-571  
*ChemPlusChem* **2015**, 80, 1408-1415.  
*RSC Advances* **2015**, 5, 83197



*Beilstein J. Org. Chem.* **2017**, 13, 182-194.  
*Exp. Opin. Drug. Deliv.* **2017**, 14 (3), 331-340.  
*Phys.Chem.Chem.Phys.* **2017**, 19, 6022-6029.  
*Phys.Chem.Chem.Phys.* **2017**, 19, 22555-563.



*Current Org. Chem.* **2018**, in press.  
*PLoS One*, **2010**, 5, e13430.  
*Photochem. Photobiol. Sci.*, **2014**, 13, 1680-1689.



*Carbohydrate Polymers* **2016**, 144, 353.

# Polysaccharide-based materials: Cellulose

## From nano-sized to NANO-STRUCTURED materials



Nanomateriali  
per la Bonifica  
associata a Dewatering  
di matrici ambientali



Regione Toscana



Nano-cellulosa  
da fonti rinnovabili per la  
somministrAzione  
sostenibile Di fitofarmaci

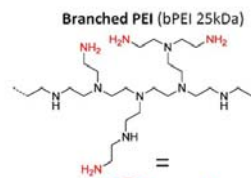
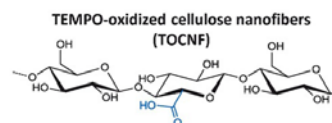
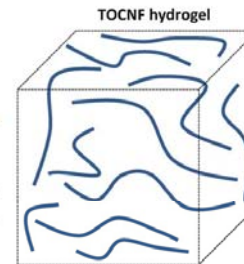
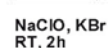
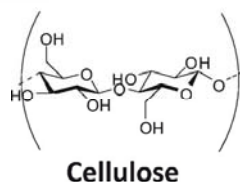


UNIVERSITÀ  
DEL SALENTO

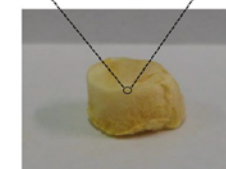
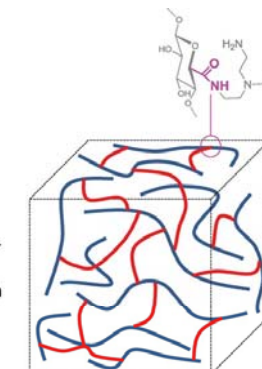


# Polysaccharide-based materials: Cellulose

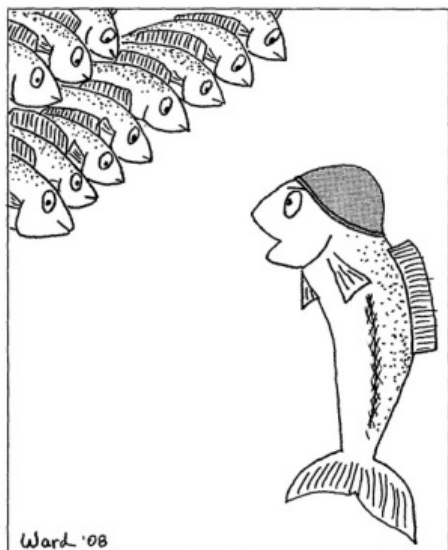
## From nano-sized to NANO-STRUCTURED materials



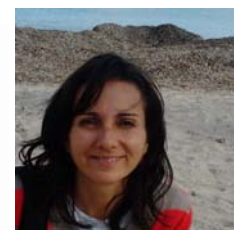
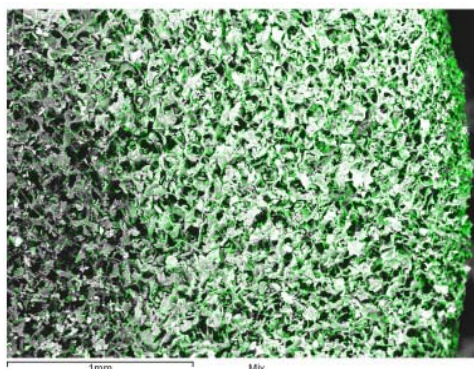
- 1) water, RT, 2h
- 2) Freeze-drying at -80°C, 24h
- 3) Heating up to 102°C, 10h



bPEI-TOCNF sponge



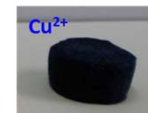
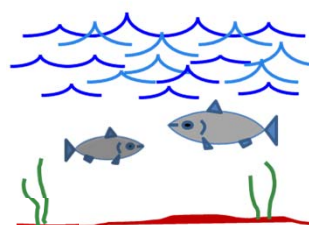
Ward '08  
Listen up men. You are about to embark on a toxicity test to determine an LC50. Look left, look right - half of you won't be coming back.



ILARIA CORSI



Water remediation



Heavy metals adsorption

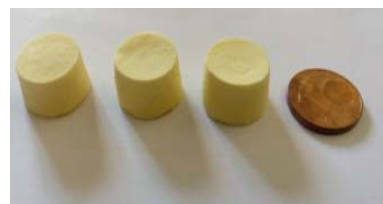
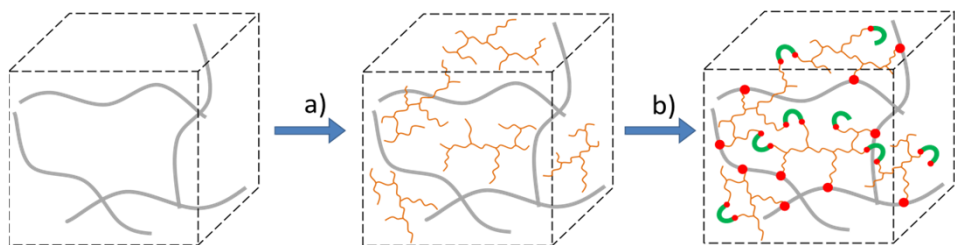
Organic pollutants adsorption

**High- capacity adsorbent - Pulp wastes - Low cost - Easy scale up - Low environmental impact**

Carbohydrate Polymers **2017**, 165, 71-85; ChemPlusChem **2017**, 82, 848-858; ChemPlusChem **2015**, 80, 1408-1415.

# Polysaccharide-based materials: Cellulose

## From nano-sized to NANO-STRUCTURED materials



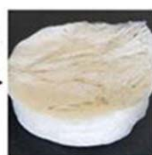
TEMPO-CNF hydrogel

XO<sub>2</sub> Sol-Gel

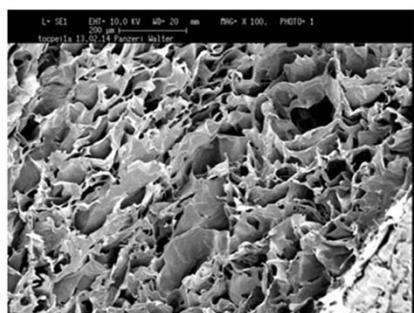


TEMPO-CNF/XO<sub>2</sub> hydrogel

freeze-drying (-80 °C)



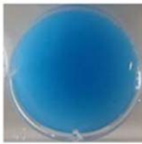
TEMPO-CNF/XO<sub>2</sub> aerogel



XO<sub>2</sub> aerogel

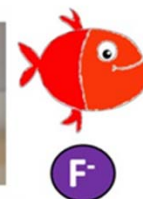
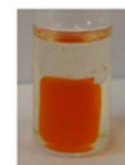
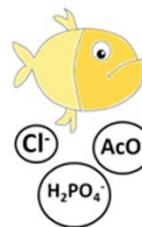
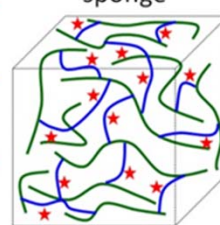
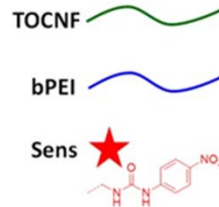


UV irradiation

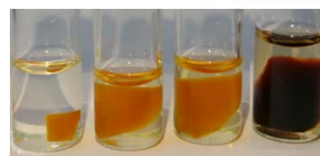


adsorption

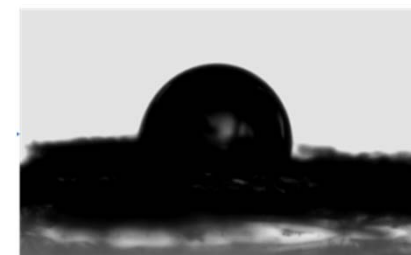
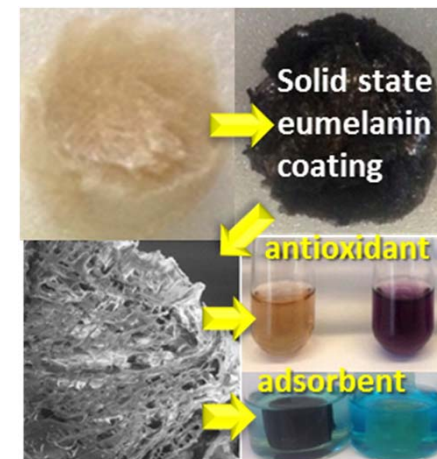
TOCNF-bPEI-Sens sponge



F<sup>-</sup> sensing



RSC Advances 2015, 5, 83197



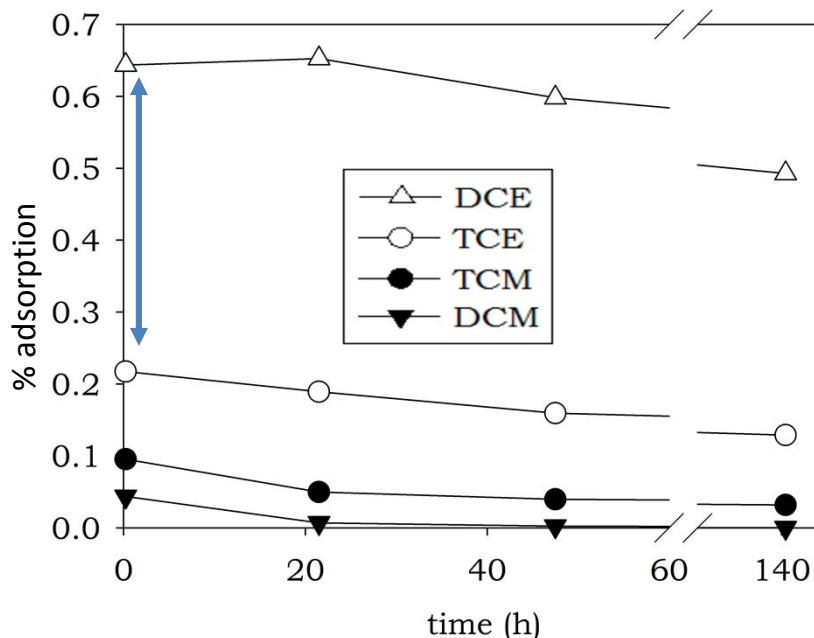
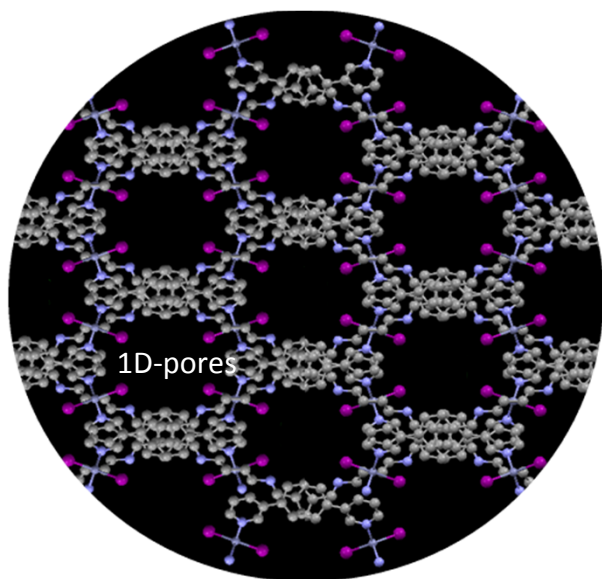
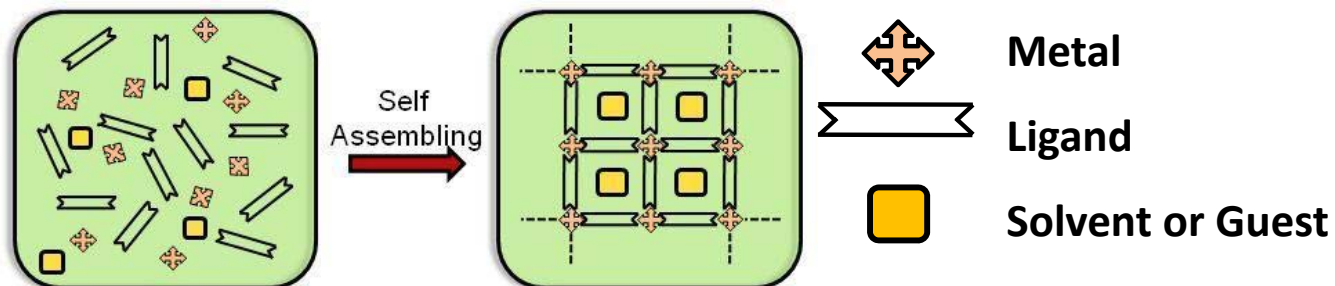
Biomacromolecules 2016, 17, 564–571

J. Photochem. Photobiol. A. 2013, 261, 53.



# Porous Coordination Polymers for novel applications: Selective Adsorption of *Volatile Organic Compounds*.

**Porous coordination polymers** are a relatively new class of hybrid materials made by the self-assembly of organic ligands and metals ions.

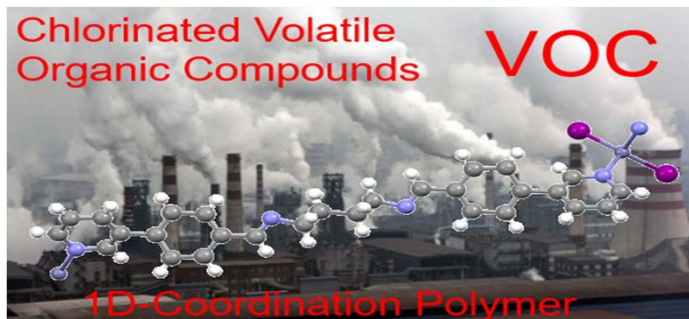


Selective adsorption of dichloro ethane (DCE) vapours over other chlorinated volatile organic pollutants under ambient conditions of T and P, and sustained retention.

*Dalton Trans.*, **2016**, 45, 18832

*Dalton Trans.*, **2016**, 45, 1674

*Chem. Commun.*, **2015**, 51, 12357



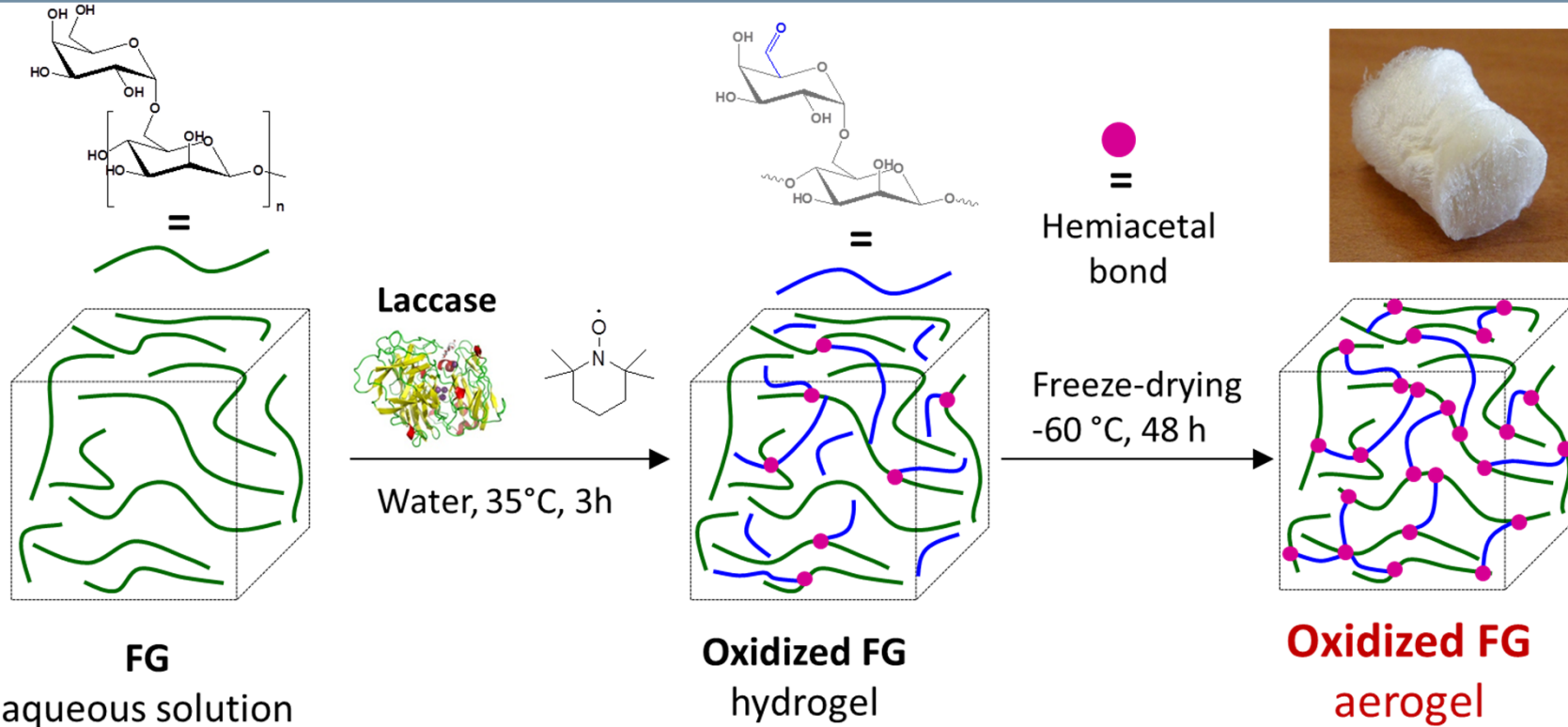
Potential applications for i) adsorption of nitro aromatics  
ii) alkane/alkene/alkyne mixture separation



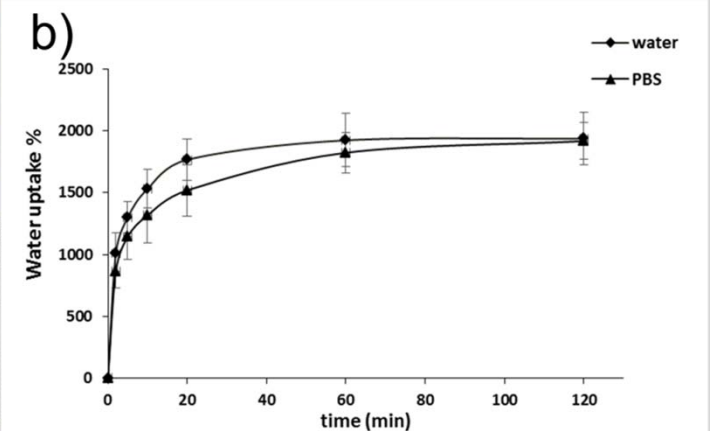
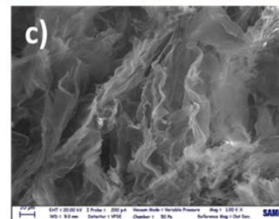
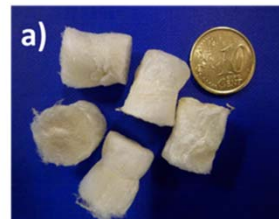
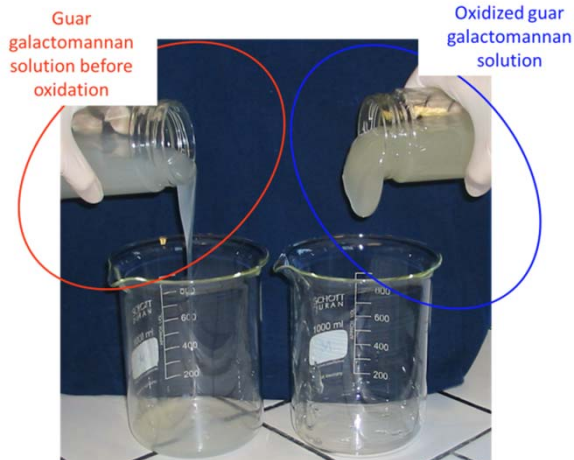


# Polysaccharide-based materials: Galactomannans

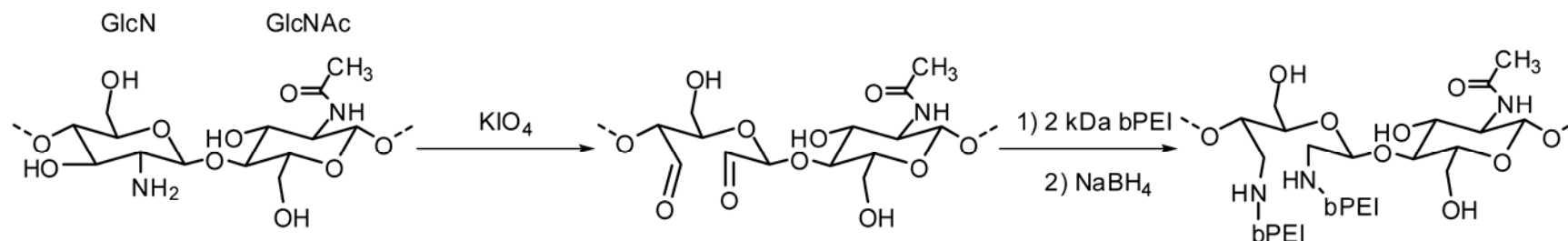
## From nano-sized to NANO-STRUCTURED materials



*Carbohydrate Polymers* **2016**, *144*, 353.



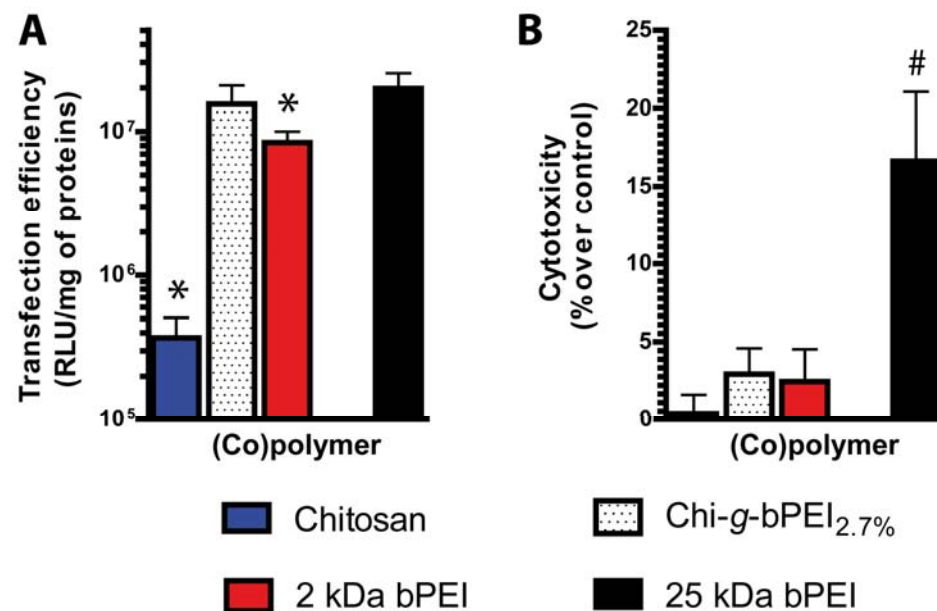
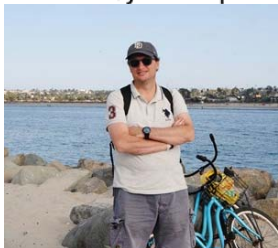
## Chitosan-Graft-PEI: efficient, non-cytotoxic, non-viral gene delivery vectors



Chi-g-bPEI <sub>x</sub> copolymer	bPEI equiv of reaction	Degree of grafting (x) <sup>a</sup>
Chi-g-bPEI <sub>0.6%</sub>	$1.27 \times 10^{-2}$	$0.6 \pm 0.1\%$
Chi-g-bPEI <sub>2.4%</sub>	$6.35 \times 10^{-2}$	$2.4 \pm 0.1\%$
Chi-g-bPEI <sub>2.7%</sub>	$1.27 \times 10^{-1}$	$2.7 \pm 0.1\%$
Chi-g-bPEI <sub>5.2%</sub>	$6.35 \times 10^{-1}$	$5.2 \pm 0.3\%$
Chi-g-bPEI <sub>7.0%</sub>	$2.54 \times 10^0$	$7.0 \pm 0.2\%$
Chi-g-bPEI <sub>8.7%</sub>	$1.27 \times 10^1$	$8.7 \pm 0.1\%$
Chi-g-bPEI <sub>8.8%</sub>	$6.35 \times 10^0$	$8.8 \pm 1.3\%$

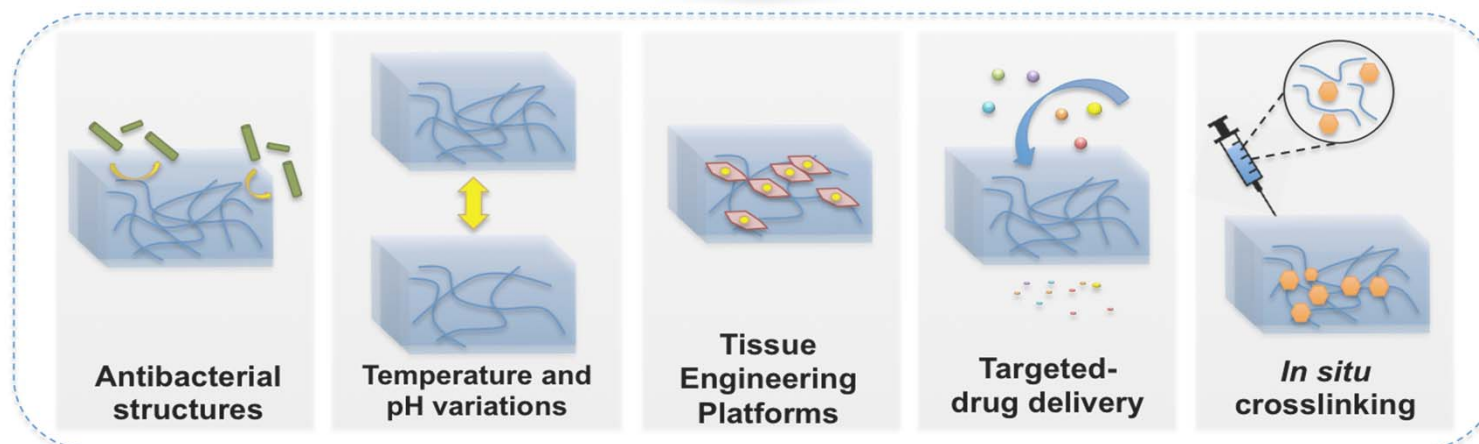
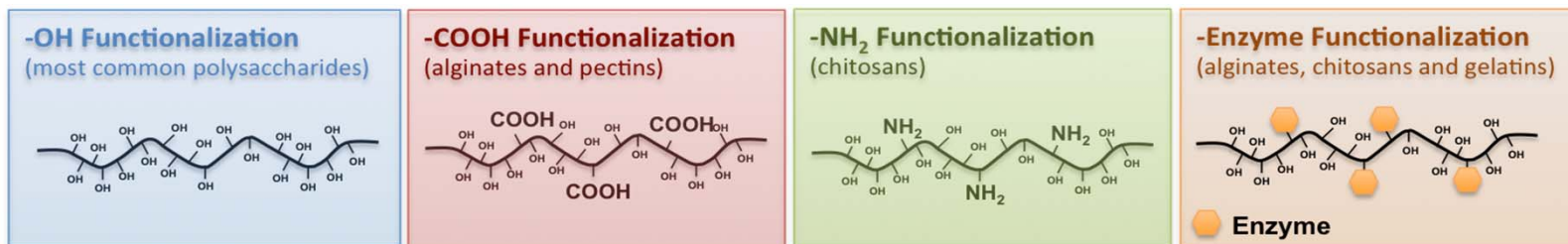
<sup>a</sup>"x" is the average percentage of D-glucosamine (GlcN) monomers grafted with branched polyethylenimine (bPEI). Results are expressed as mean  $\pm$  standard deviation.

doi:10.1371/journal.pone.0034711.t001



*PLoS One*, 2010, 5, e13430; *Photochem. Photobiol. Sci.*, 2014, 13, 1680–1689

# Polysaccharide-based materials: Chitosan



*Current Org. Chem.* **2018**, in press.

*PLoS One*, **2010**, 5, e13430; *Photochem. Photobiol. Sci.*, **2014**, 13, 1680–1689

# Oligosaccharide-based materials: Cyclodextrin (CD) and Cyclodextrin Nanosponges (CDNS)

✓ natural and biodegradable compounds

✓ low toxicity and high versatility

## Home care



## Food



## Cosmetics



## Drugs



# New catalytic systems for sustainable oxidations

**Why:** oxidative processes of organic compounds represent some of the most important chemical transformations involved in many fundamental areas, including general synthesis, industrial processes, materials, energy, biology, and so on.

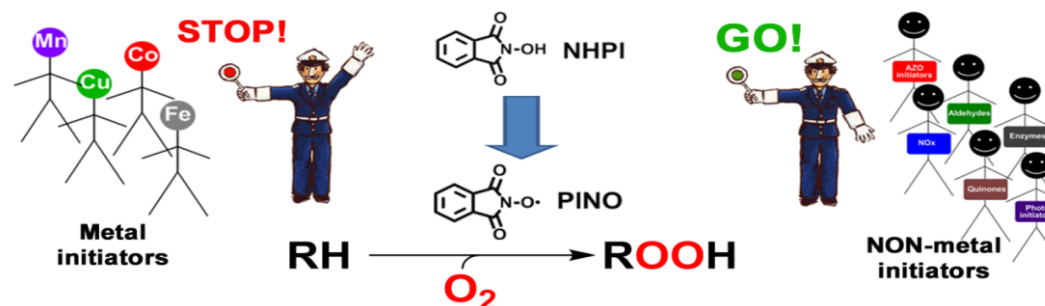
**The oxidants:** the eco-friendly standards for the oxidative processes require oxidants able to combine a low environmental impact with an economical convenience. Molecular oxygen and hydrogen peroxide are the ideal oxidants from this point of view.

**Catalysis:** the use of these green oxidants strictly depends on the employment of catalytic systems, which allow operating with high selectivity under mild conditions.

This group is specialized in the design of new – often metal-free – homogeneous catalytic systems for the selective oxidation of a wide range of substrates.

The developed processes based on this new catalysts often provide promising “green” and more convenient alternatives to classical industrial procedures

More than 20 papers on the field  
4 book chapters edited by Wiley & Elsevier  
5 international patents  
2 national patents



*Beilstein J. Org. Chem.* 2013, 9, 1296-1310.

# OSCMLab – Laboratory of Organic Synthesis, Catalysis, and Materials



*Prof. Alessandro Sacchetti*



*Prof. Alessandro Volonterio*



*Prof. Massimo Cametti*



*Prof. Carlo Punta*



*Dr. Melone, PhD*



*Dr. Fiorati, PhD*



*Dr. Petroselli, PhD*



*Dr. Pastori*



*Dr. Rossi, PhD*



*Dr. Pennetta*



*Dr. Rossetti*



*Dr. Colombo Dugoni*

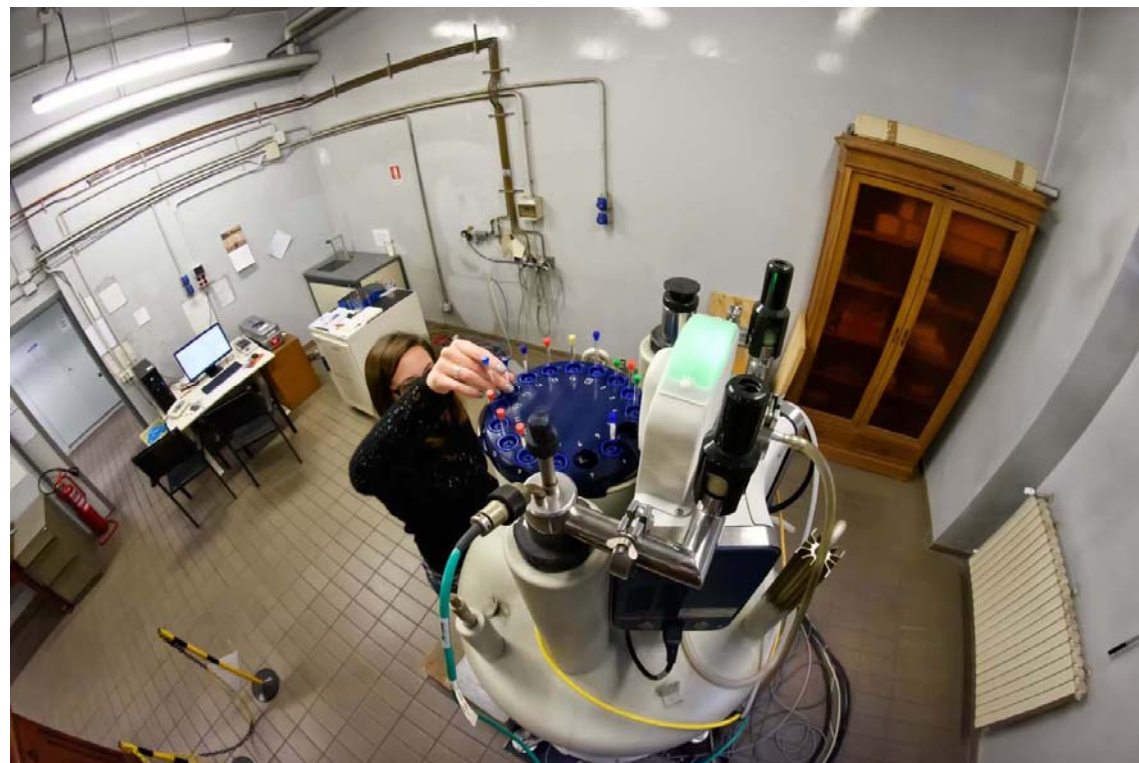


*Dr. Caruso*



*Dr. Lippi*

# LGS – Laboratorio Grandi Strumenti



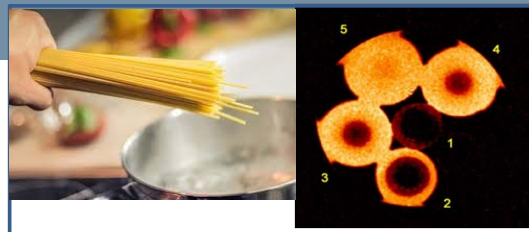
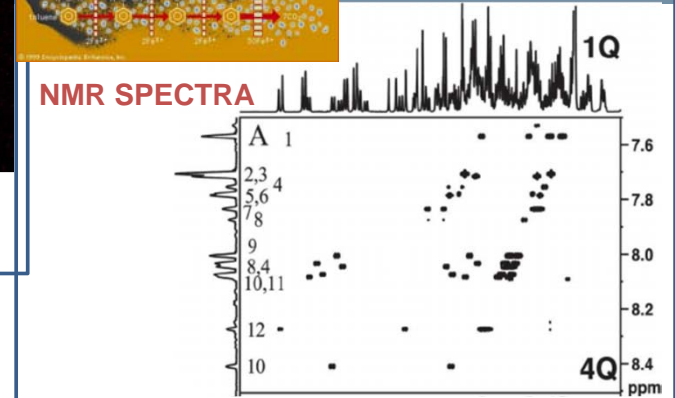
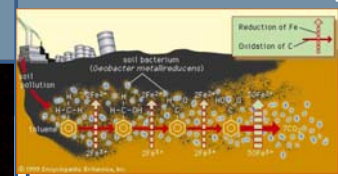
**NMR spectroscopy  
Mass Spectrometry  
Powder X-ray Diffraction  
FT-IR -UV-Vis  
Freeze-drying equipment**

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# LGS – What can NMR do for you?

## How to identify pollutants?



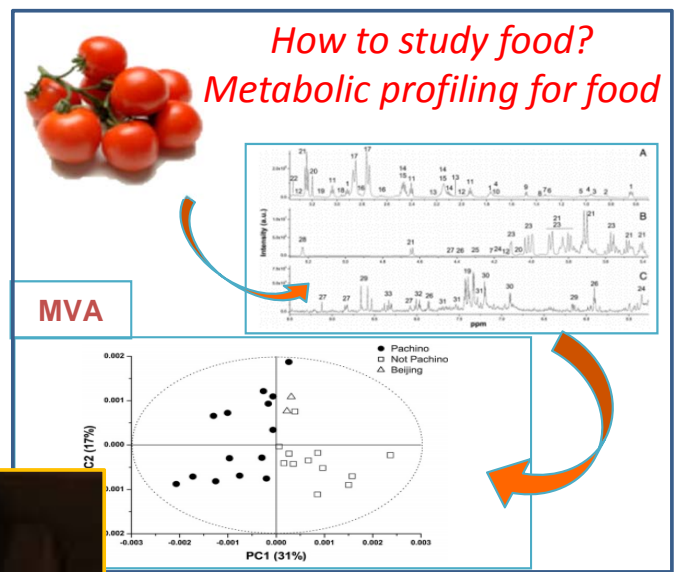
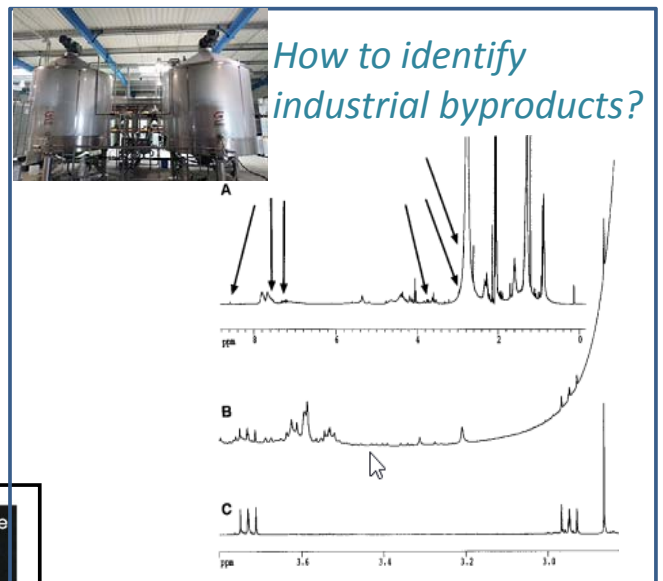
NMR microimaging of cooked pasta

**LIQUID STATE**  
From molecular structure to metabolomics

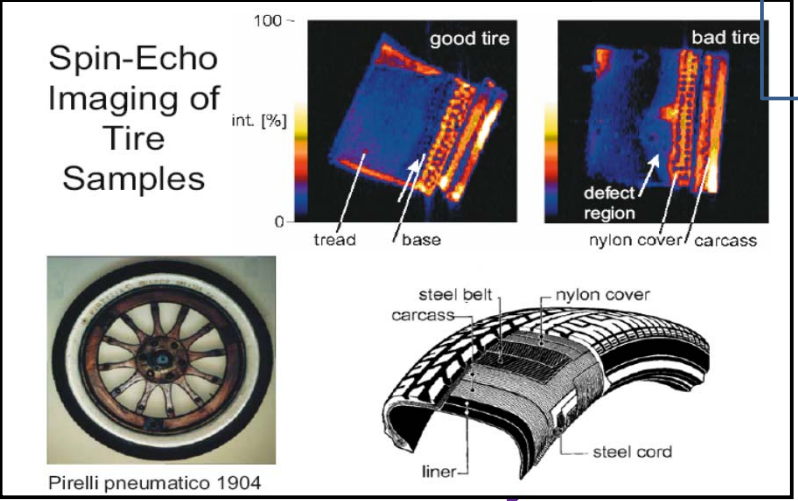
**SOLID STATE**  
From materials to drug delivery

**SOFT MATTER**  
Gels, Composites, Suspensions

**MICROIMAGING**  
From medicine to materials engineering



## How to evaluate materials?



What's inside a gel?  
Cosmetics and Wellness Products