Towards Next-Generation Catalyst: Nano-Scale Heterogeneity and Structural

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CPAC Rome Workshop 2026

Rome (I), March 23-25, 2026

Our research group

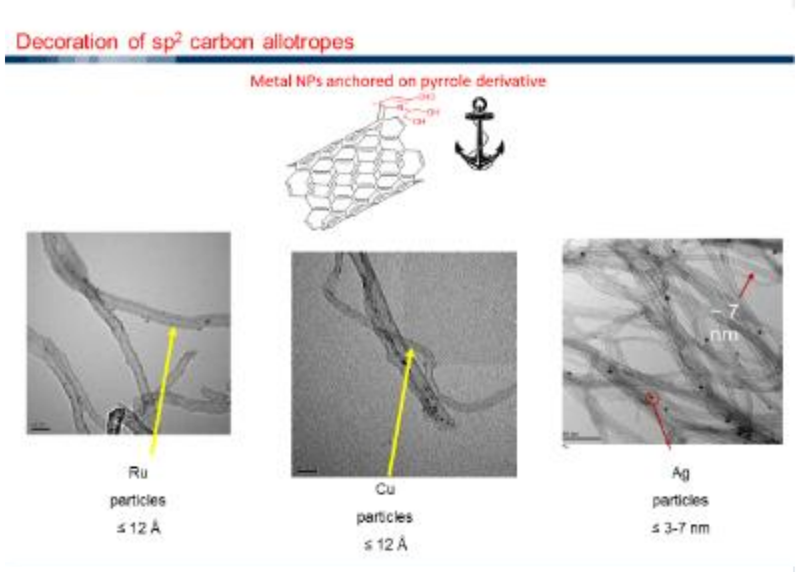
ISCaMaP

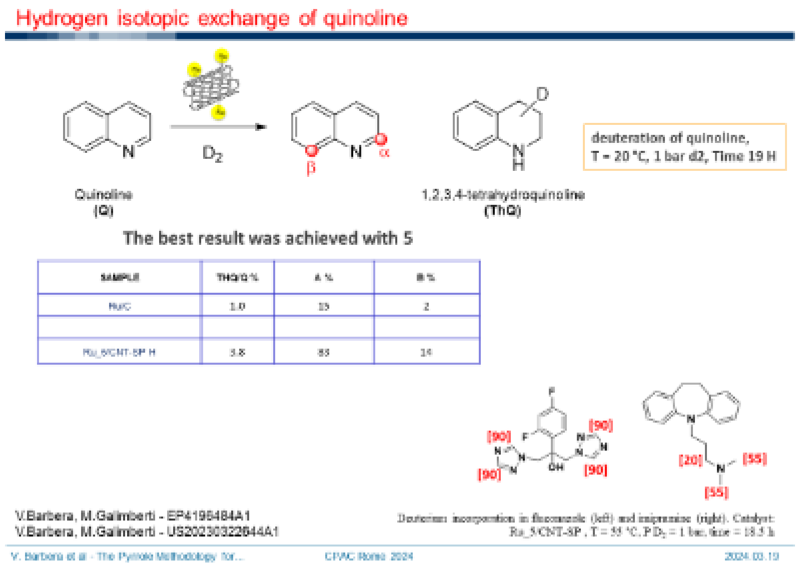
Innovative Sustainable Chemistry and Materials and Proteins Group

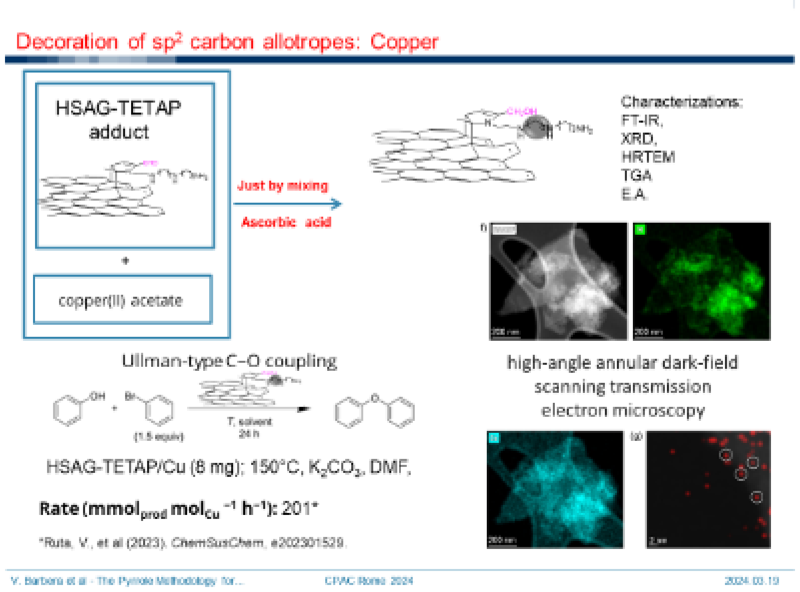
Innovative
Sustainable
Materials
GROUP
in ISCaMaP

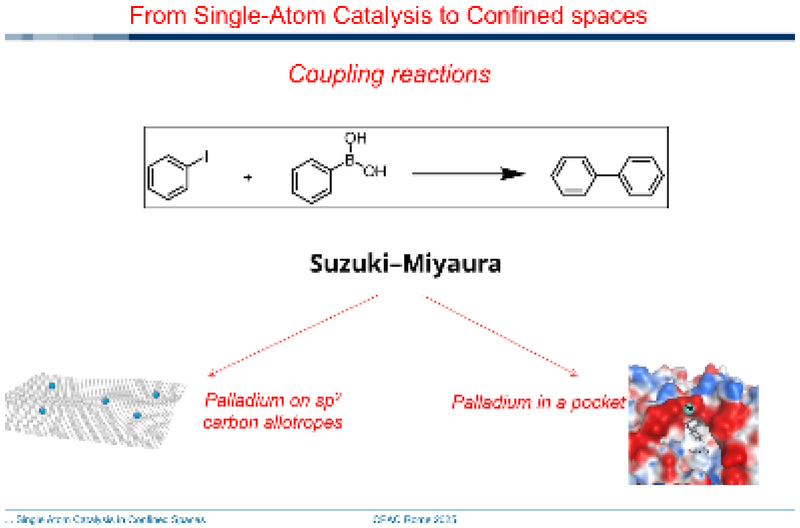
Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering “G. Natta”

Previous CPAC workshops



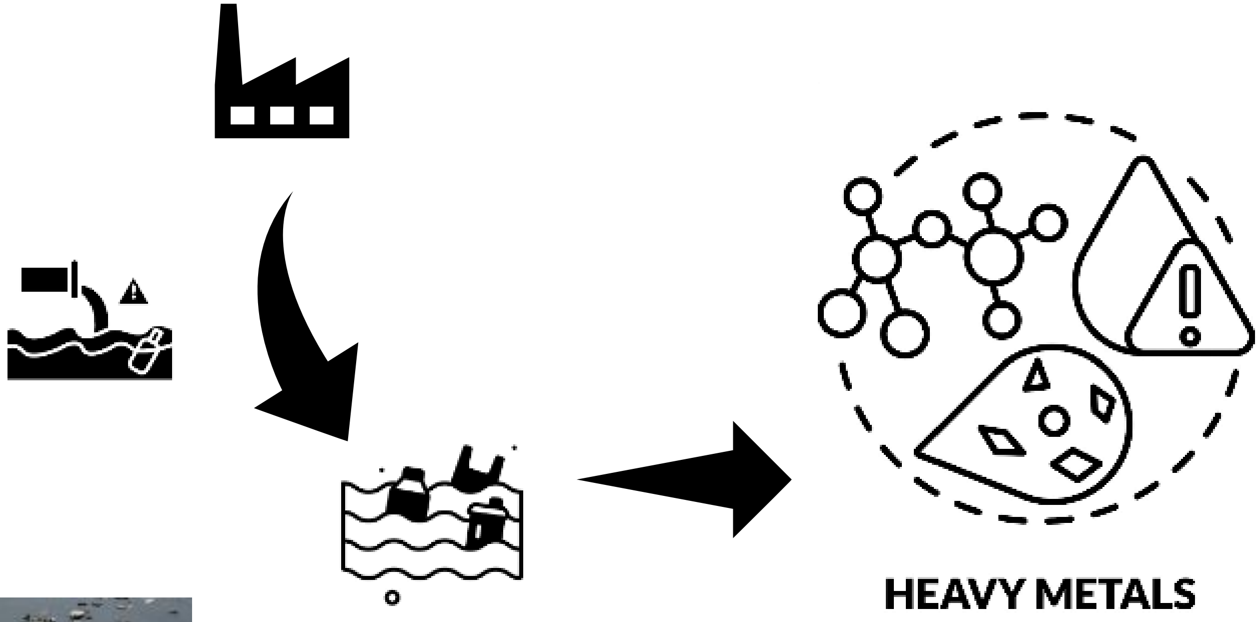




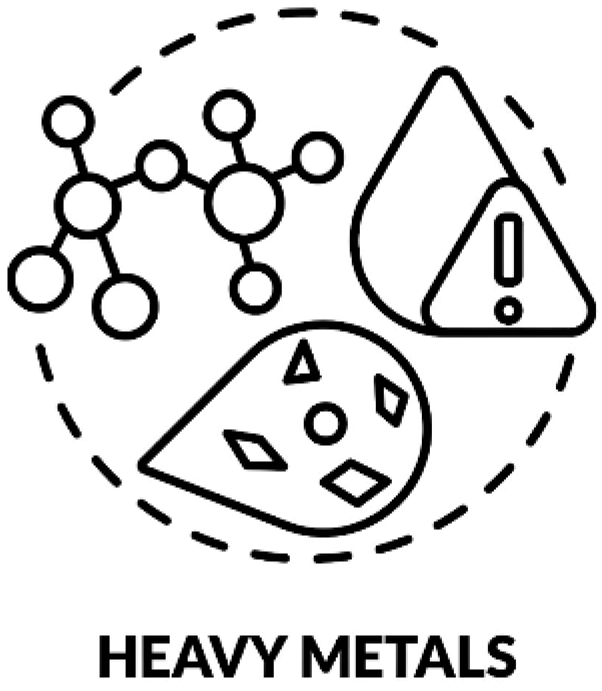


With greetings from Prof Vincenzina Barbera!!

Heavy metal water pollution

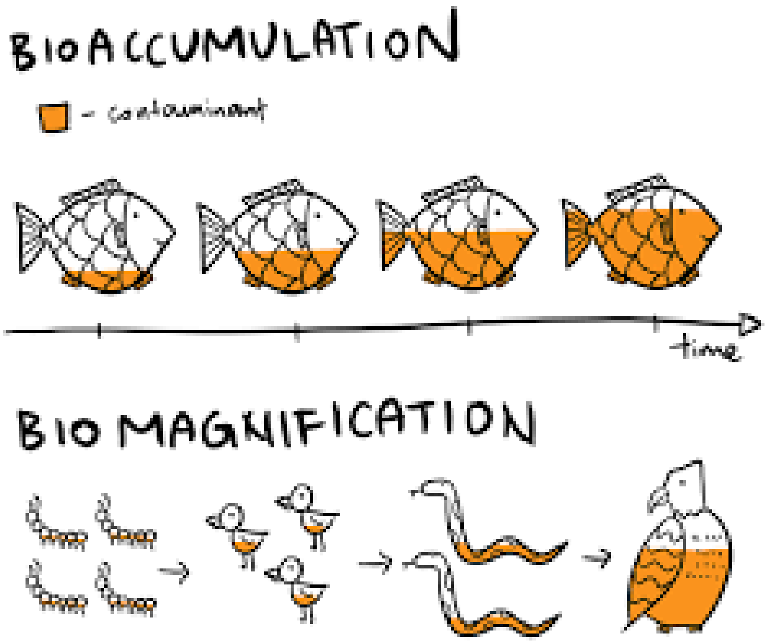


Heavy metal water pollution



Bioaccumulation and Biomagnification

Heavy metals do not degrade. They accumulate in the tissues of aquatic organisms and increase in concentration as they move up the food chain, reaching humans.



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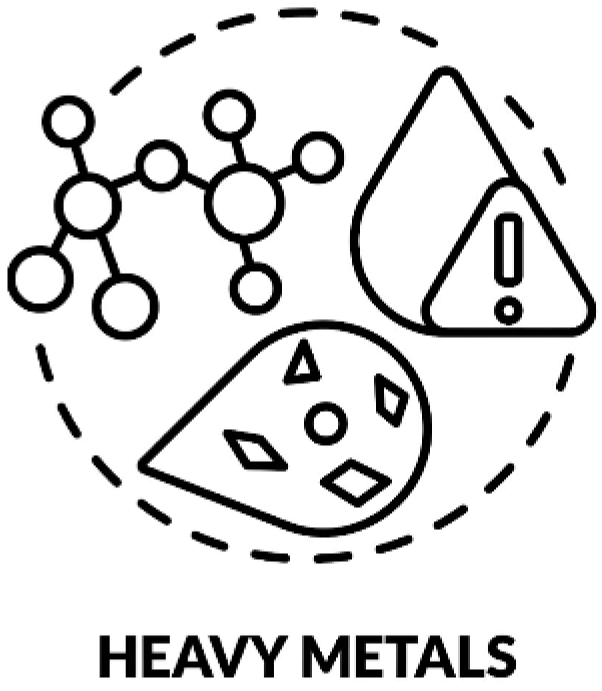
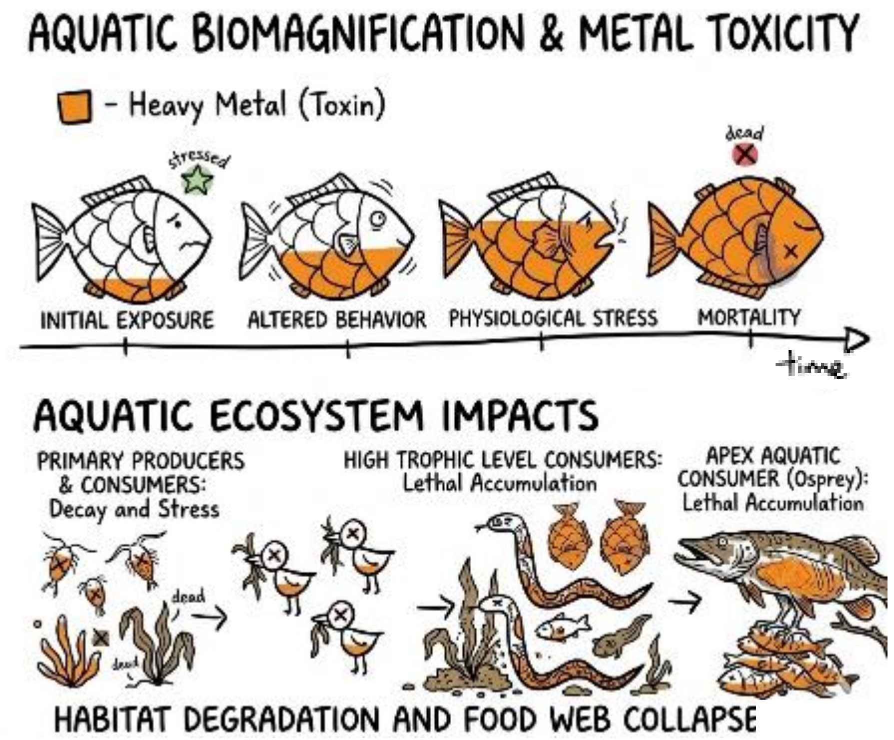
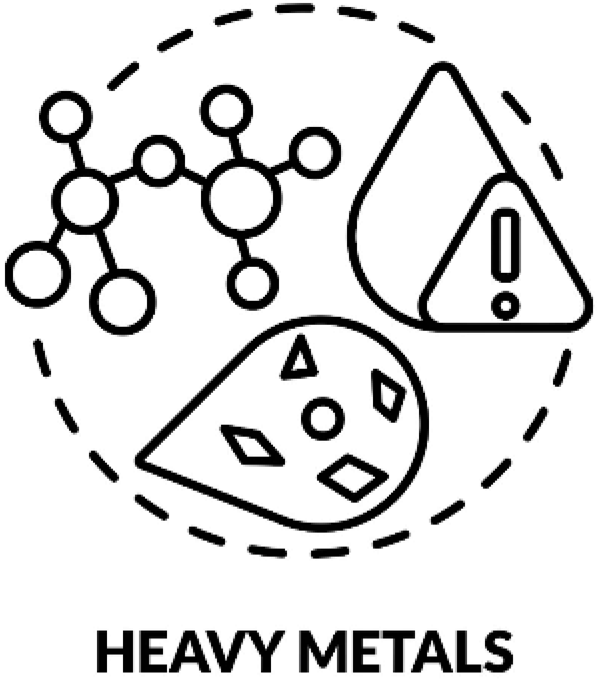


Toxicity to Aquatic Life

Metals can disrupt the reproduction, growth, and survival of fish and amphibians, leading to a loss of biodiversity.



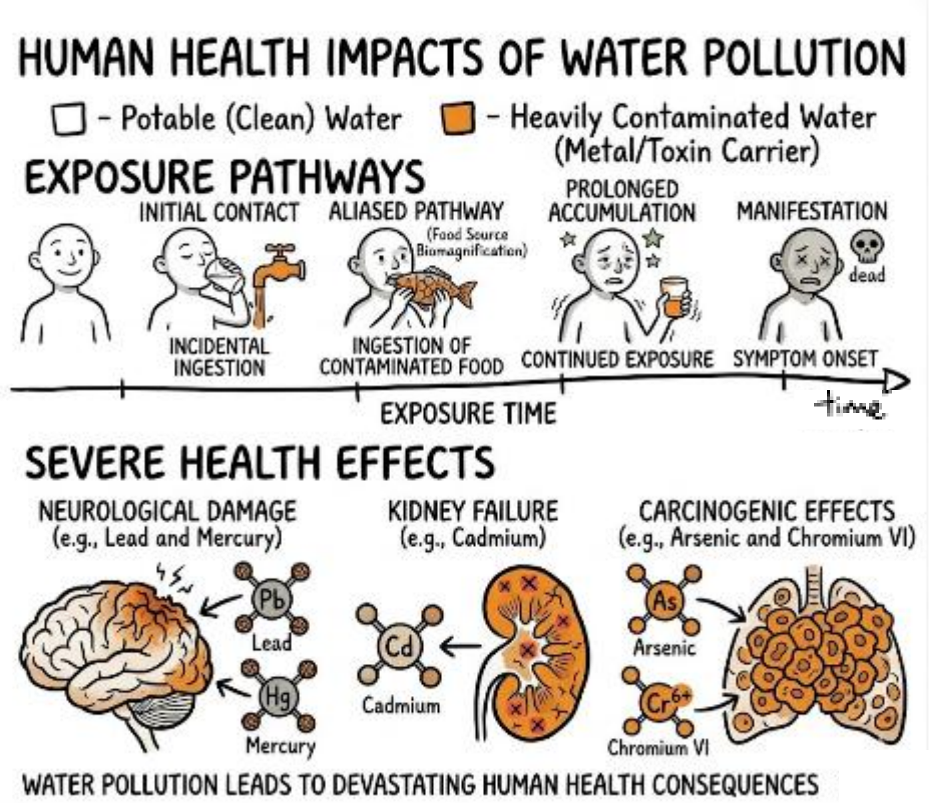
Heavy metal water pollution



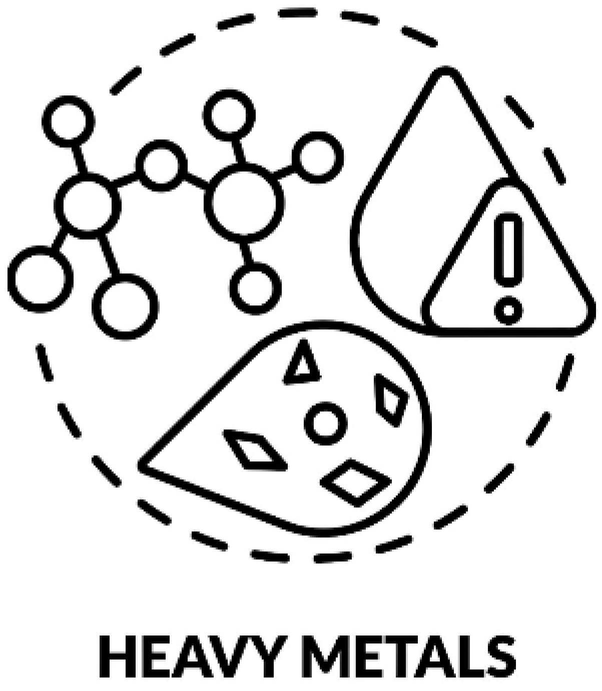
Human Health Risks

Exposure through drinking water or contaminated food can cause severe conditions, including:

- Neurological damage (e.g., Lead and Mercury).
- Kidney failure (e.g., Cadmium).
- Carcinogenic effects (e.g., Arsenic and Chromium VI).



Heavy metal water pollution

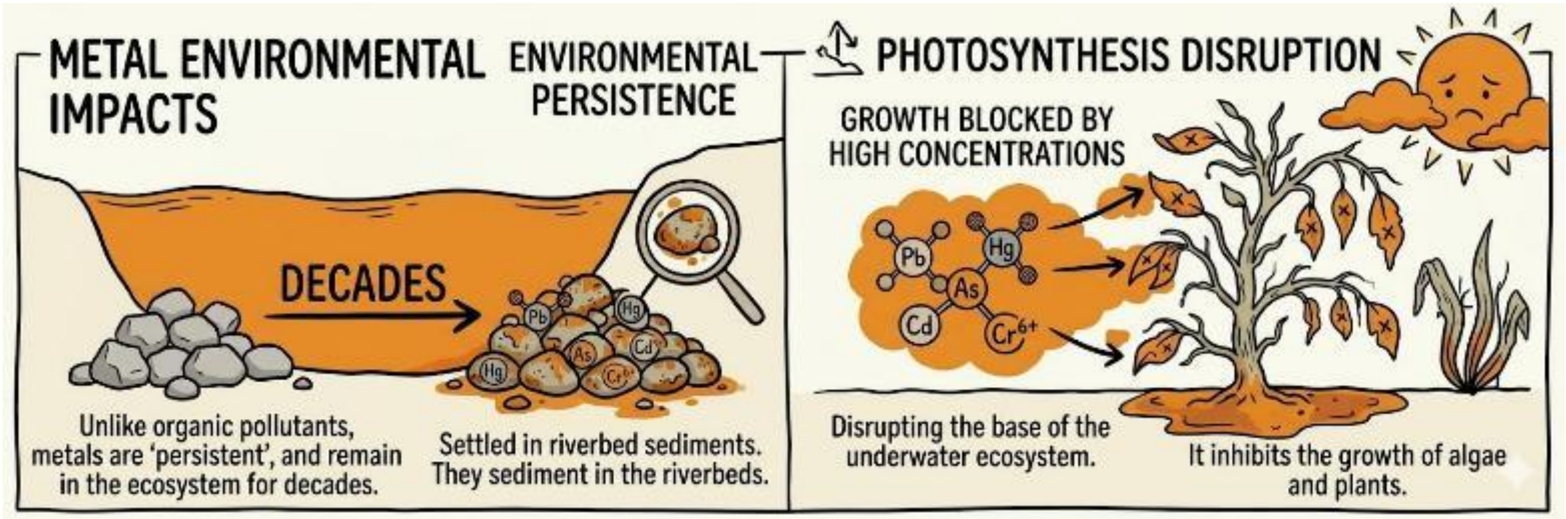


Persistence in the Environment

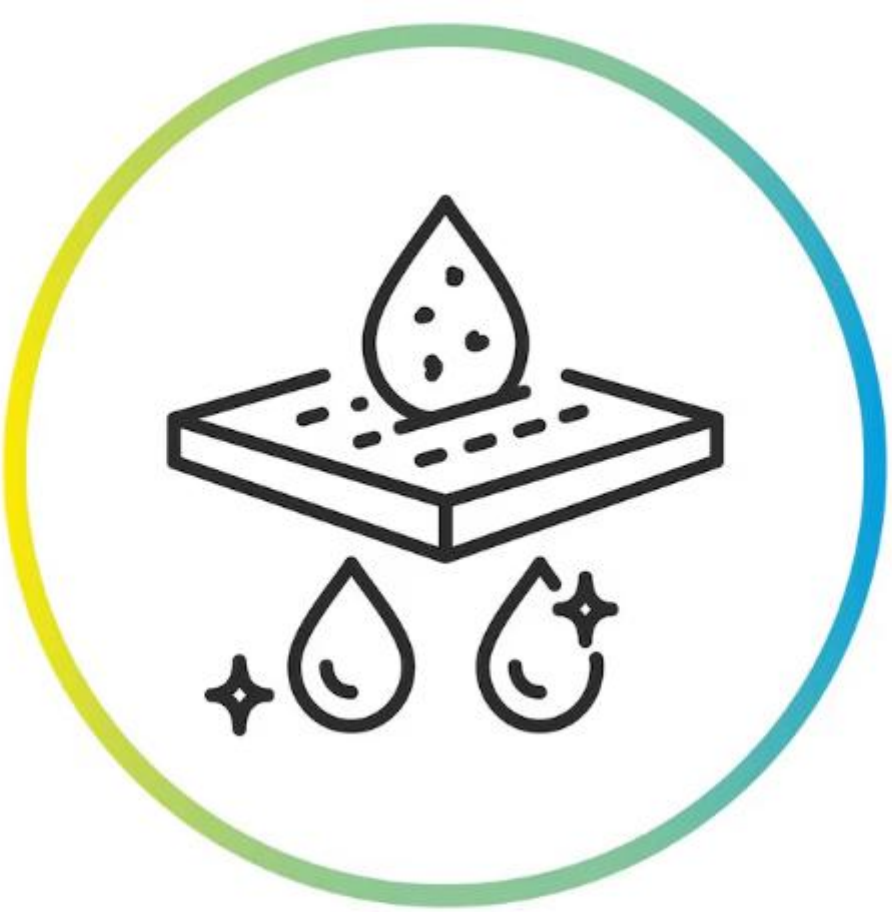
Unlike organic pollutants, metals are "persistent," meaning they remain in the ecosystem for decades, settled in riverbed sediments.

Disruption of Photosynthesis

High concentrations of metals in water can inhibit the growth of algae and aquatic plants, disrupting the base of the underwater ecosystem.

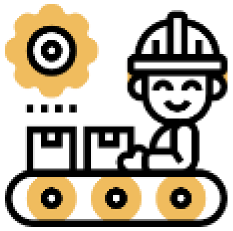


Heavy metal water pollution

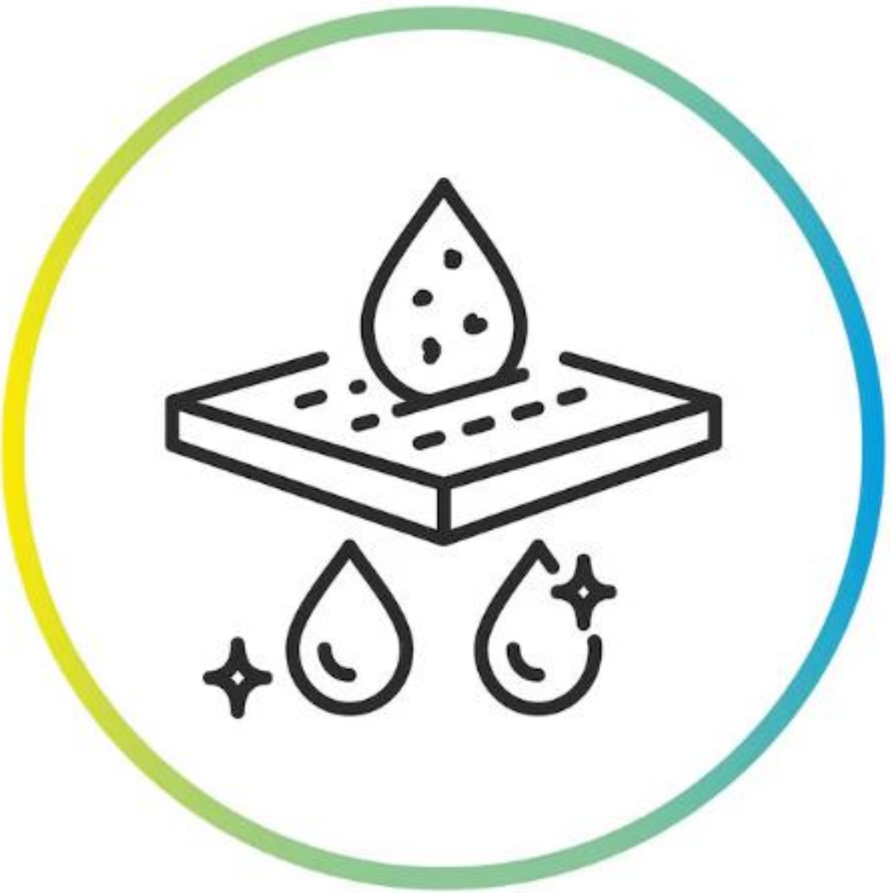


Challenges and Limitations of Water Filtration Systems

- High Capital and Operational Costs: Implementation and maintenance require significant financial investment.
- Complex Manufacturing Process: Production involves sophisticated technology and specialized materials.

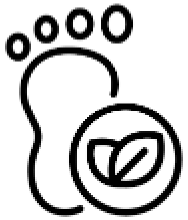


Heavy metal water pollution

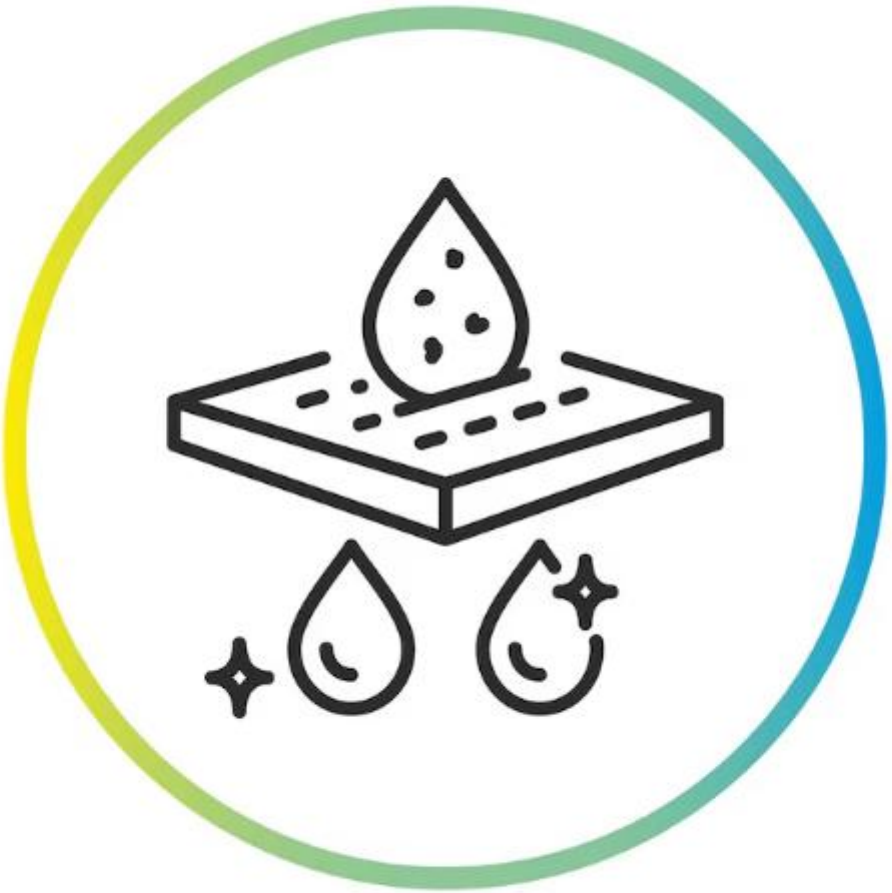


Challenges and Limitations of Water Filtration Systems

- Non-Recyclable Components: Many filter cartridges and membranes are made of composite materials that cannot be easily recycled.
- Significant Environmental Footprint: The lifecycle of filters contributes to plastic waste and resource depletion.

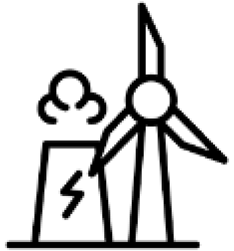


Heavy metal water pollution



Challenges and Limitations of Water Filtration Systems

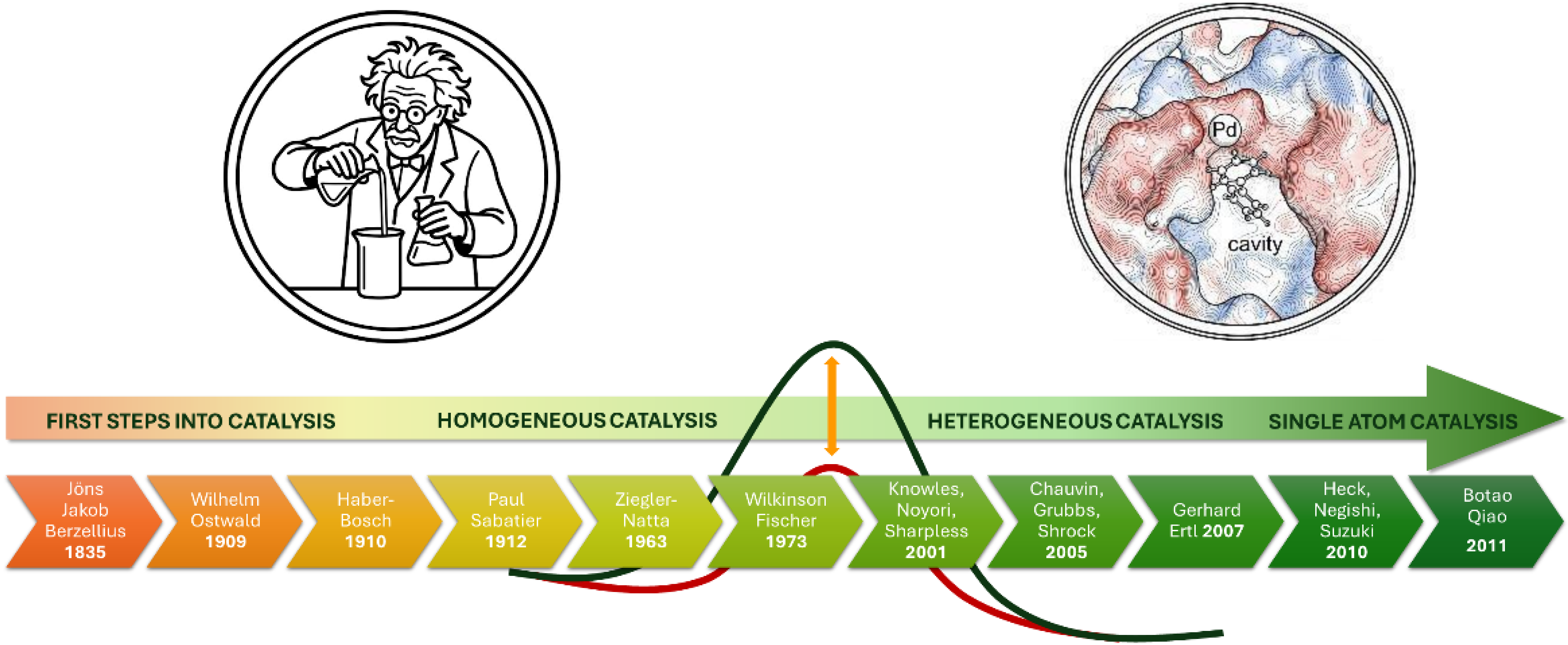
- Frequent Replacement Requirements: Limited lifespan leads to high turnover and continuous waste generation.
- Energy-Intensive Production: The manufacturing of advanced filtration media (like reverse osmosis membranes) requires substantial energy.



Heavy metals: Not always a heavy burden.

Every metal has a silver lining.

Evolution of Catalysis: From Origins to Modern Frontiers

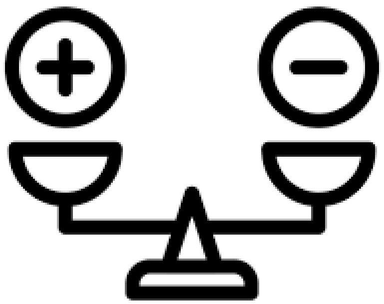


V. Barbera, A. Ravicini, D. Allevi. One catalyst to rule them all: a journey from bulk to atom-level control. VOL. 43(3) - MAY / JUNE 2025 | CATALYSIS 2 July 2025

Homogeneous Catalysts

PROS

- **High Selectivity:** Uniform active sites (single-site) ensure precise chemical transformations.
- **High Activity**: Excellent interaction between reactants and catalyst due to the same phase.
- **Easy Characterization**: Molecular structures are well-defined and easy to study via NMR/IR.
- **Mild Conditions:** Often operates at lower temperatures and pressures.



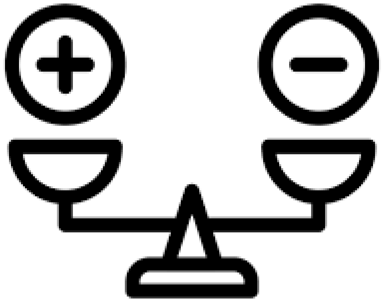
CONS

- **Difficult Separation:** Catalyst recovery from the product stream is complex and expensive.
- **Low Thermal Stability:** Organometallic complexes often decompose at high temperatures.
- **High Catalyst Loss:** Irreversible leaching of expensive precious metals or ligands.
- **High Environmental Footprint:** Large amounts of solvents/energy needed for catalyst recycling.

Heterogeneous Catalysts

PROS

- **Easy Separation**: The solid catalyst is easily filtered or decanted from liquid/gas products.
- **Continuous Operation:** Ideal for large-scale flow reactors and industrial applications.
- **High Thermal Stability:** Can withstand harsh reaction conditions and high temperatures.
- **Long Catalyst Life:** Easier to regenerate and reuse multiple times.



CONS

- **Lower Selectivity:** Multiple types of active sites on the surface can lead to side products.
  - **Mass Transfer Issues**: Reaction rates are often limited by diffusion into catalyst pores.
  - **Sintering & Coking**: High-temperature deactivation via particle aggregation or carbon deposits.
- **Surface Complexity**: Difficult to map and understand the exact nature of the active sites.

Bridging the Gap: A Circular Economy Approach

Turning Water Contaminants into Catalytic Opportunities

The Challenge

Homogeneous Pollution: Metals in wastewater are hazardous and difficult to recover.

Heterogeneous Synthesis: Preparing solid catalysts is often resource-heavy and expensive.

Bridging the Gap: A Circular Economy Approach

The Dual-Use Strategy

Step 1: Remediation (The Adsorption Phase)

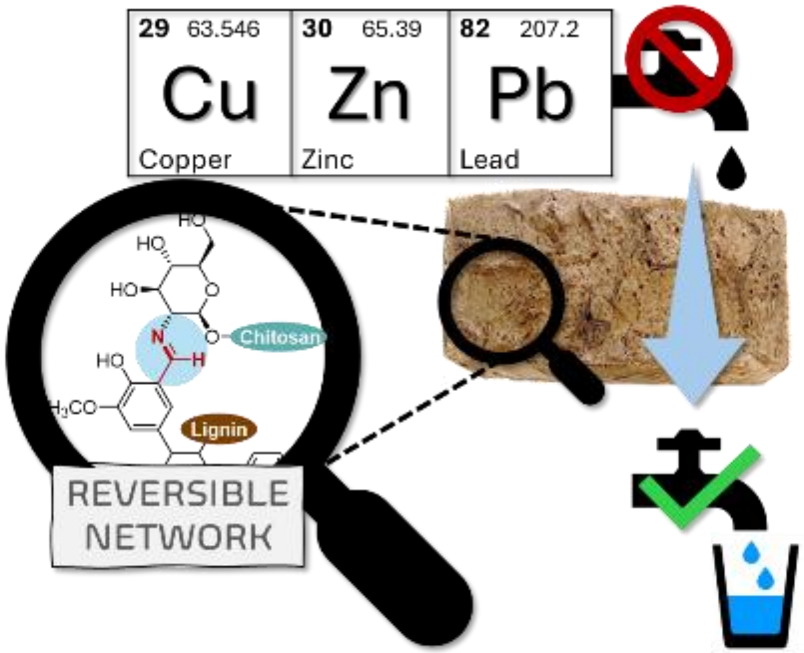
The "Burden": Scavenging toxic heavy metals from aqueous streams.

The Result: Clean water + a metal-loaded solid material.

Step 2: Valorization (The Catalytic Phase)

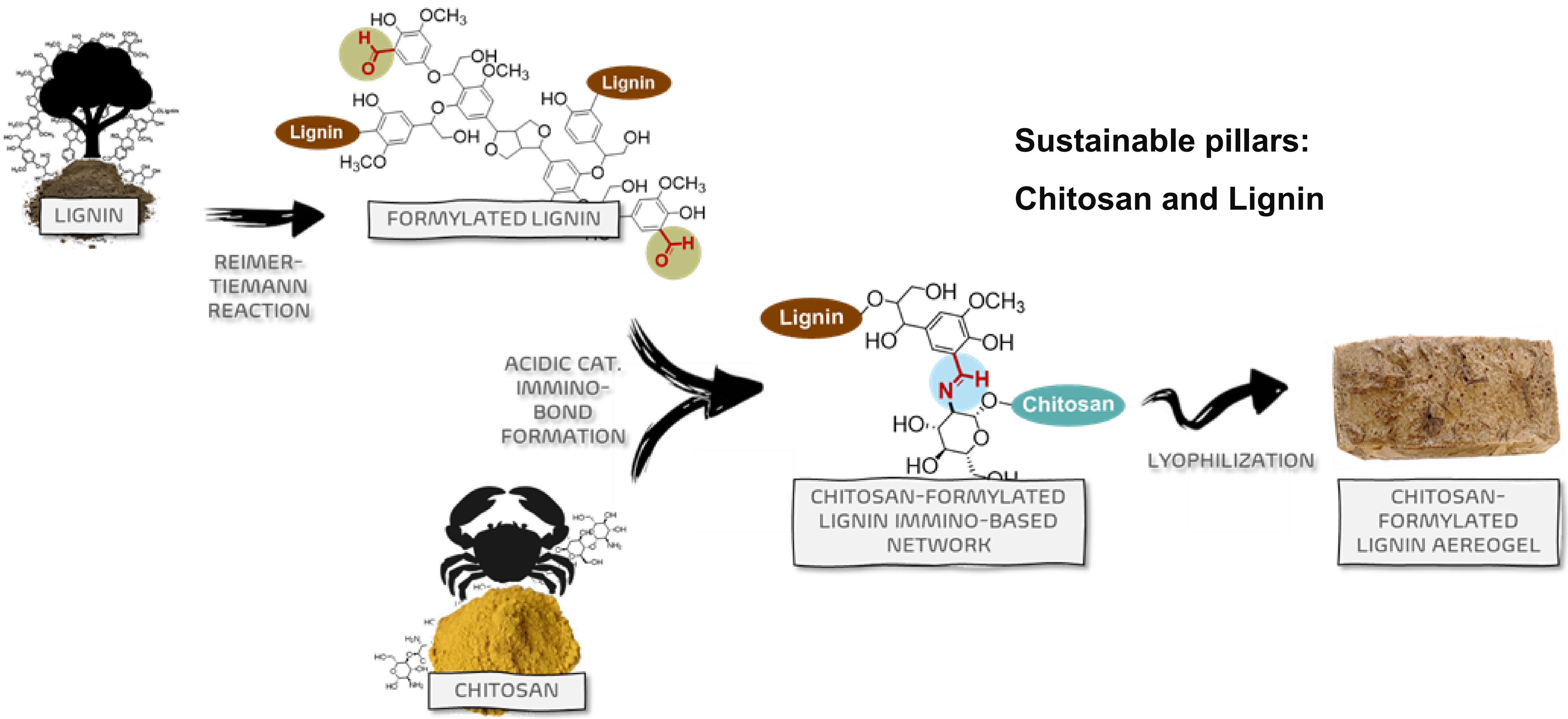
The "Silver Lining": The adsorbed metals are repurposed as **active sites**.

The Result: A heterogeneous catalyst for sustainable synthesis.



We don't just "clean" the water; we **harvest** the catalyst

Aim of the work



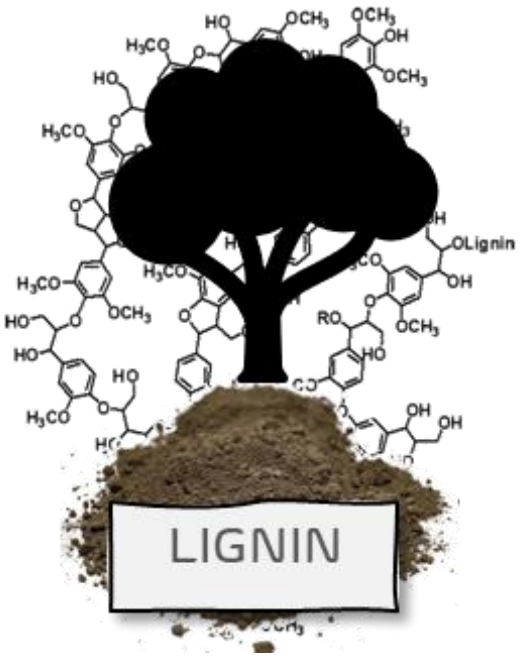
Sustainable pillars:

Chitosan and Lignin

D. Gentile, D. Allevi, M. Zambito Marsala, L. Criscuolo, M. Galimberti, V. Barbera. Smart Materials for Dirty Waters: Reversible Aerogels Unlock Closed-Loop Heavy Metal Remediation, Small Science, 2026.

Sustainable sources

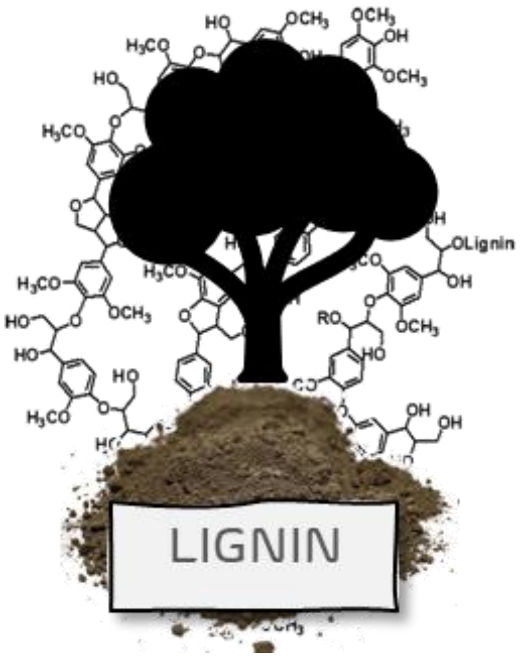
Why lignin?



- **Polyphenolic Groups**: Lignin is the largest natural source of aromatic compounds. Its structure is packed with phenolic hydroxyl and methoxy groups.
- **Amorphous Three-Dimensional Network**: Its complex, cross-linked structure provides high mechanical strength and thermal stability, acting as a sturdy "scaffold" for the adsorbent.
- **Hydrophobic/Hydrophilic Balance**: The aromatic rings provide a degree of hydrophobicity, while the functional groups allow interaction with aqueous pollutants, making it versatile for different reaction environments.
- **High Carbon Content:** Its aromatic nature makes it an excellent precursor for carbon-based catalysts and supports.

Sustainable sources

Why lignin?



- **Pulp and Paper Industry By-product**: It is a major waste product of the paper industry (often burned for low-value energy). Valorizing it for water treatment follows the Circular Economy principles.
- **Abundant Terrestrial Resource**: After cellulose, lignin is the most abundant renewable carbon source on Earth, ensuring a stable and low-cost supply chain.
- **Chemical Robustness:** Unlike many other biopolymers, lignin is naturally resistant to microbial degradation and chemical attack, which translates to a longer catalyst lifespan in harsh conditions.

Sustainable sources

Why chitosan?

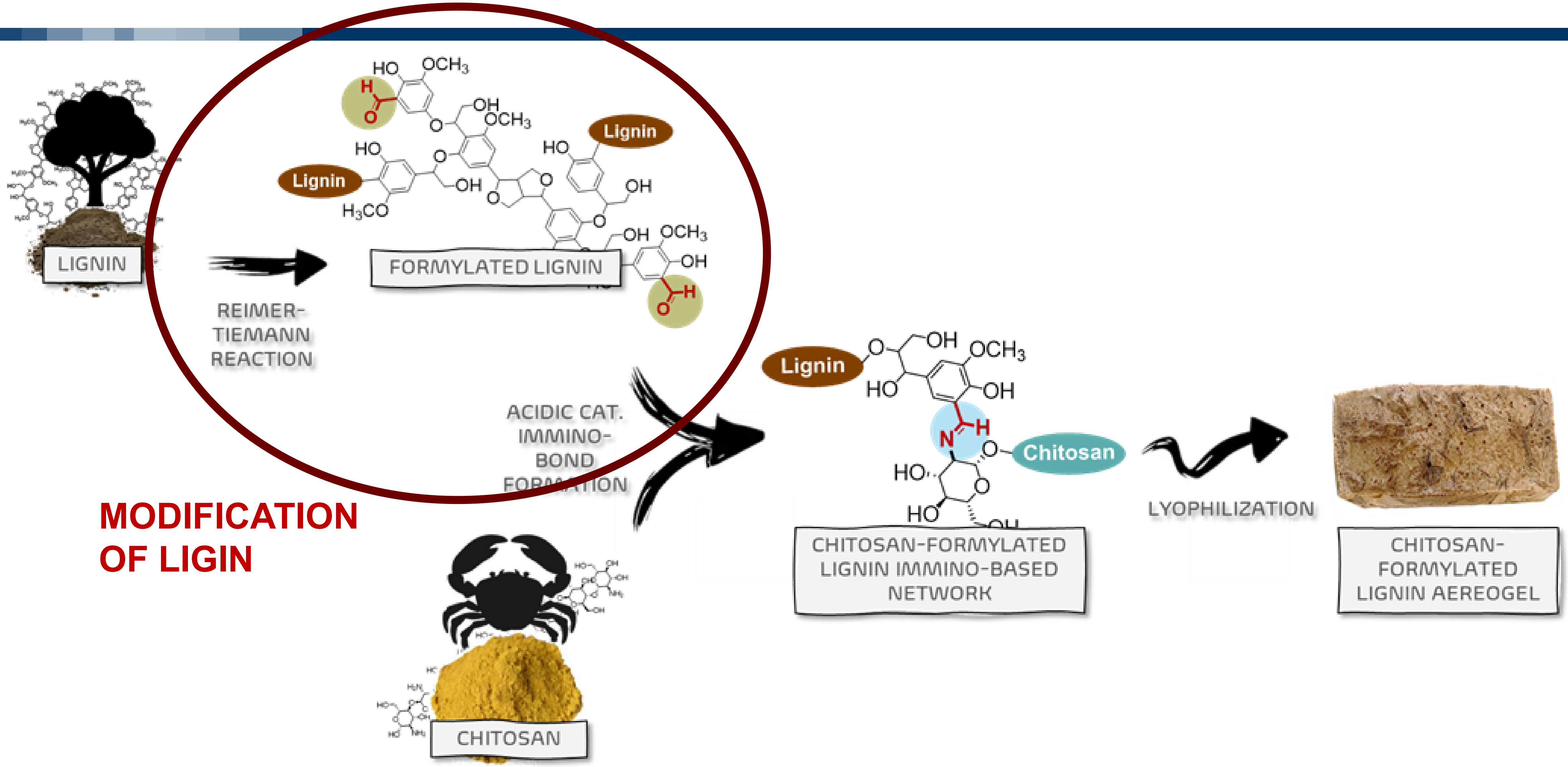
- **Abundant Amino Groups (-NH_2):** The high density of primary amino groups along the polymer chain provides re-active sites for the chelation of heavy metal ions.
- **Presence of Hydroxyl Groups (-OH):** Alongside amino groups, these facilitate hydrogen bonding and further chemical functionalization, allowing you to "tune" the adsorbent.
- **Film and Bead Forming Ability:** It can be easily processed into different physical forms (flakes, beads, membranes, or nanofibers) depending on the reactor requirements.

Sustainable sources

Why chitosan?

- **Waste Valorization**: It is derived from chitin (from crab and shrimp shells), the second most abundant natural biopolymer on Earth.
- **Biodegradability**: Unlike synthetic polymers (plastics), chitosan is broken down by specific enzymes (like lysozymes) into non-toxic glucosamine units, ensuring no long-term environmental persistence.
- **Biocompatibility and Non-toxicity**: It is safe to handle and does not introduce secondary toxicity.

Aim of the work



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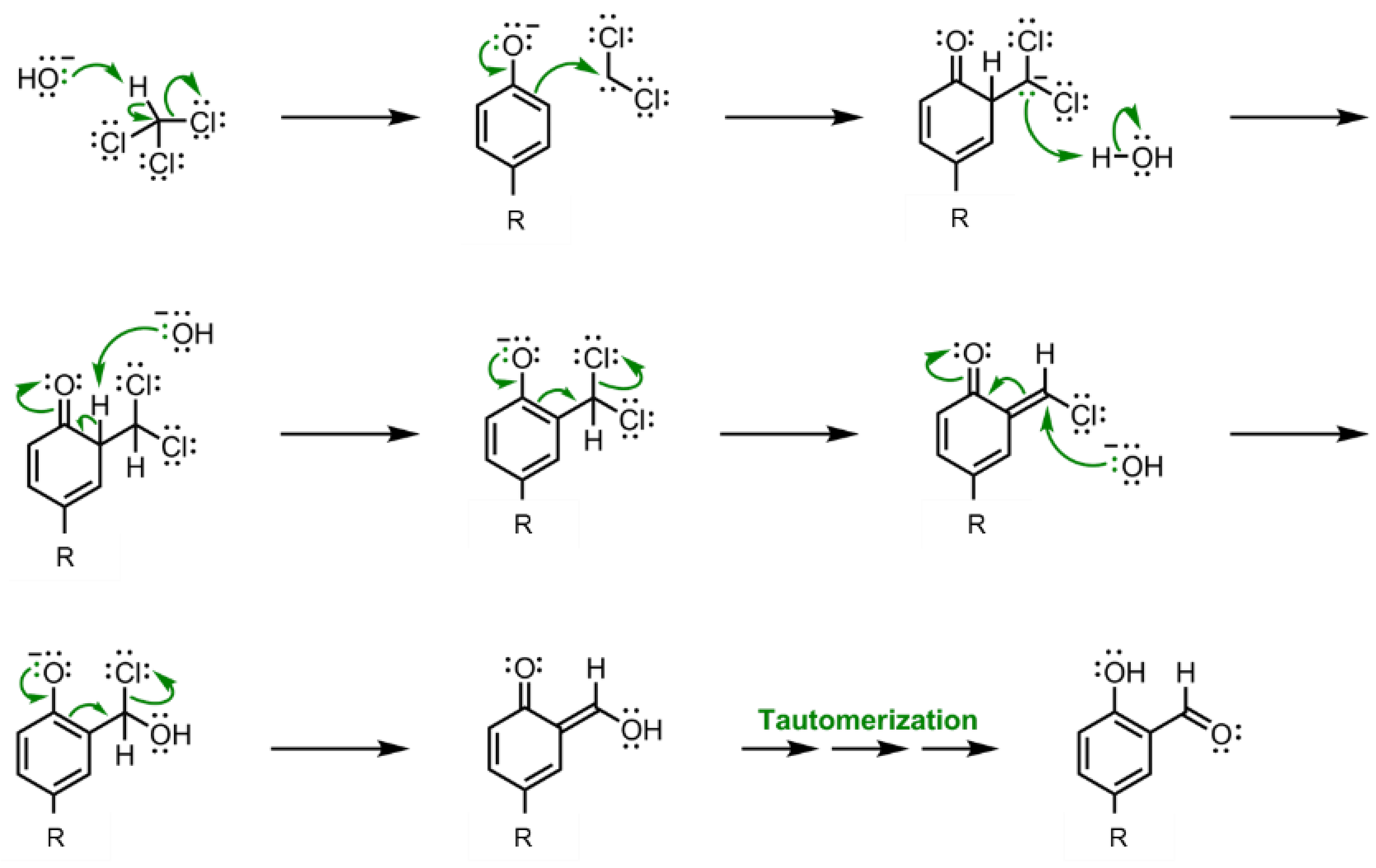
Lignin modification: Reimer Tiemann

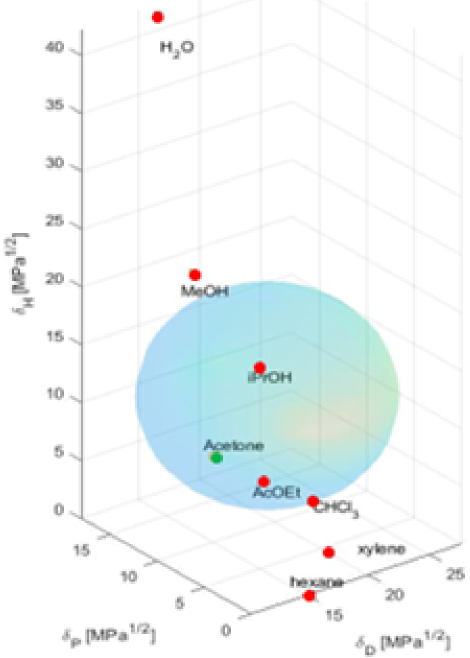


Reimer Tiemann reaction on lignin. R = lignin main chain

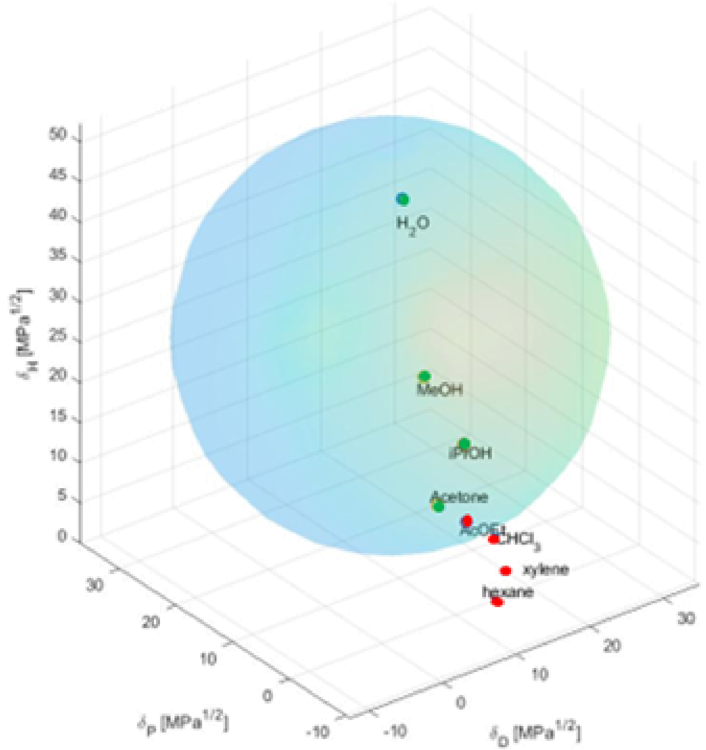
Formylated lignin (LGN-CHO) Pristine lignin (LGN)

Tollens' test for confirmation: Silver mirror in the presence of aldehydic groups on lignin

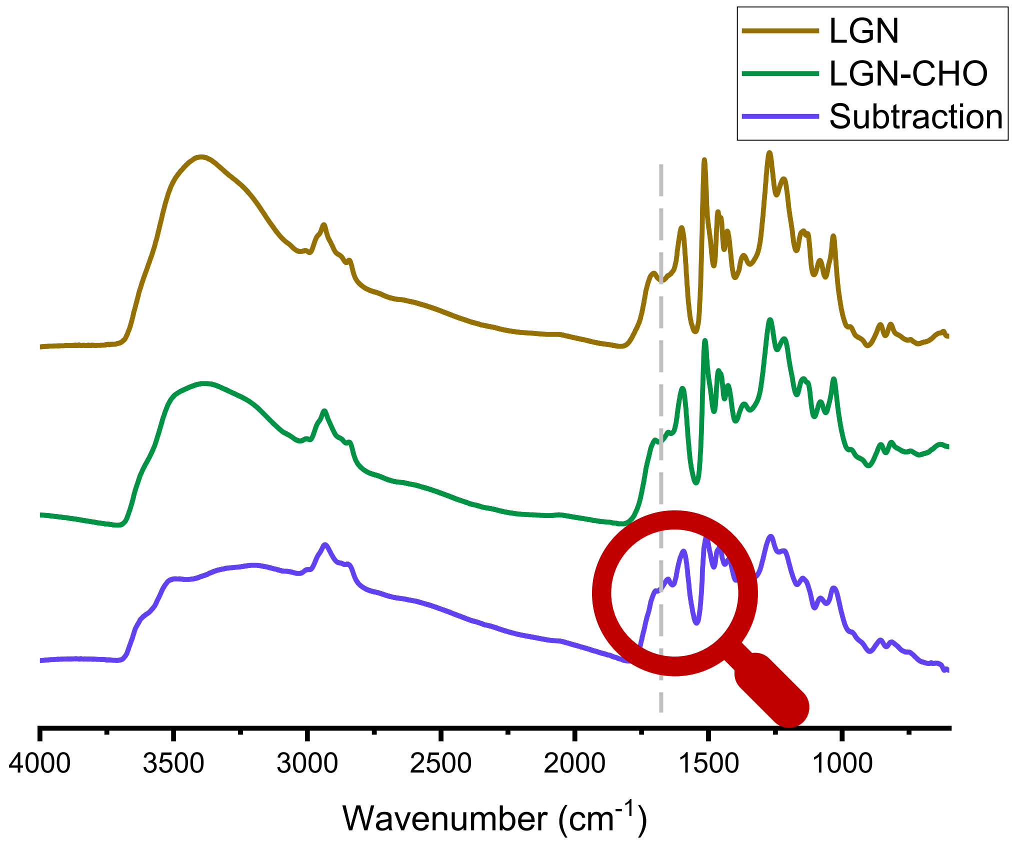
Modified lignin characterization



LGN



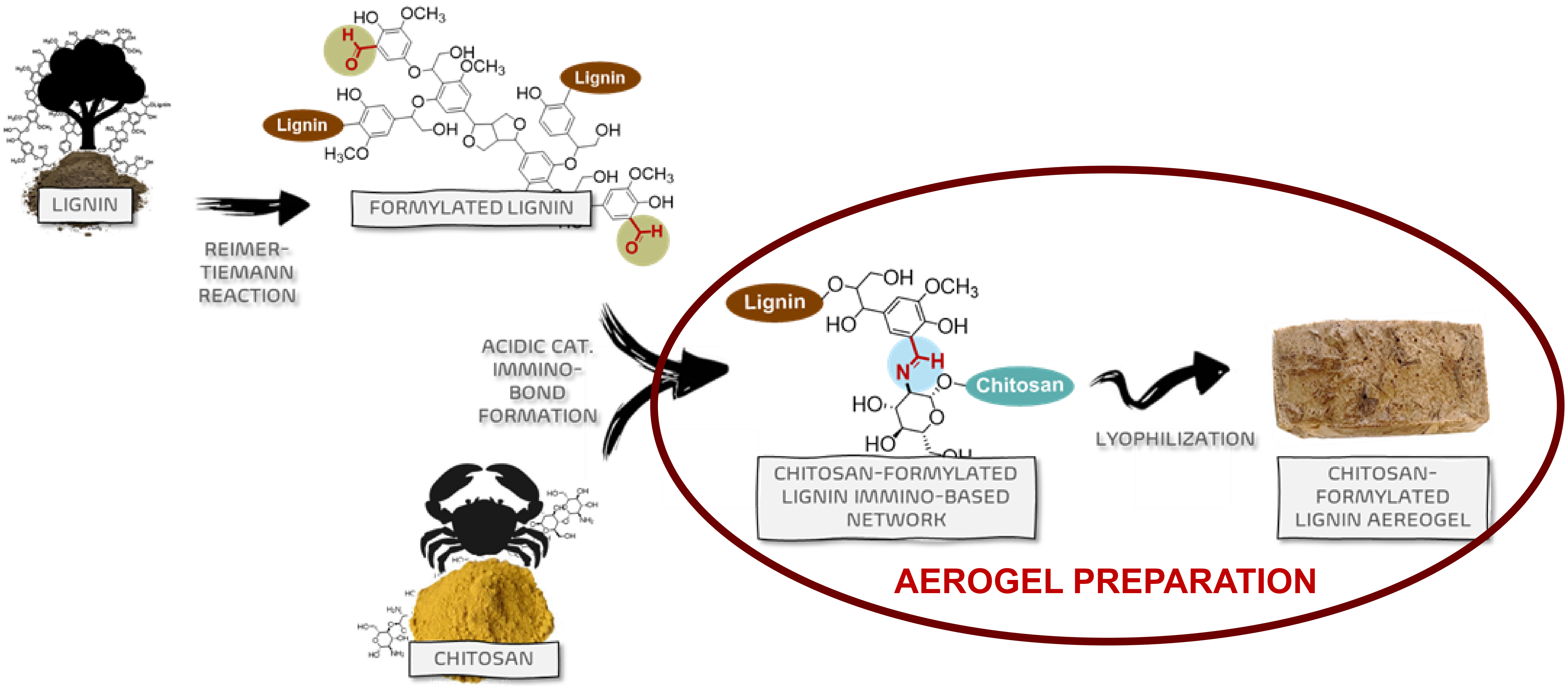
LGN-CHO



Hansen sphere: formylated lignin is more soluble than pristine lignin.

Infrared spectroscopy: a peak at 1650 cm^{-1} indicates the presence of aldehydic group

Aim of the work



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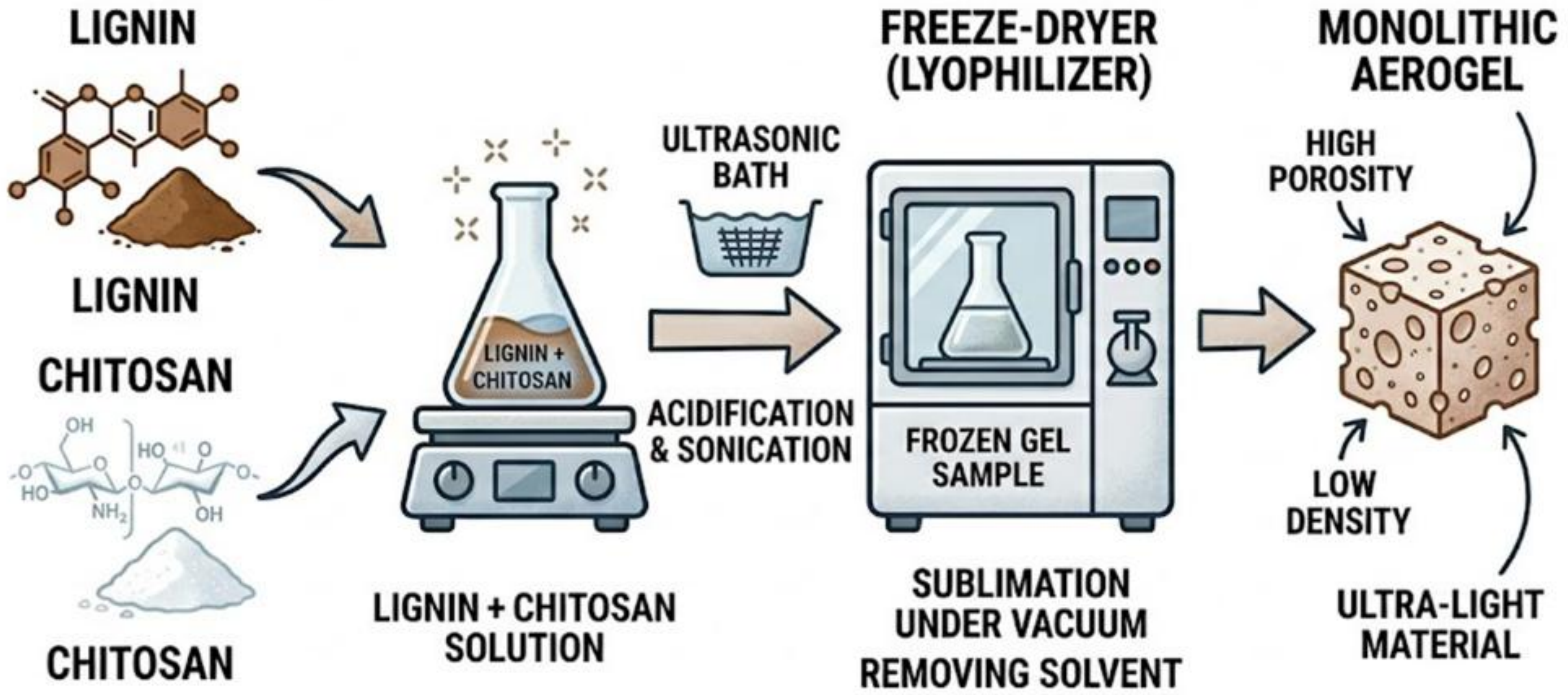
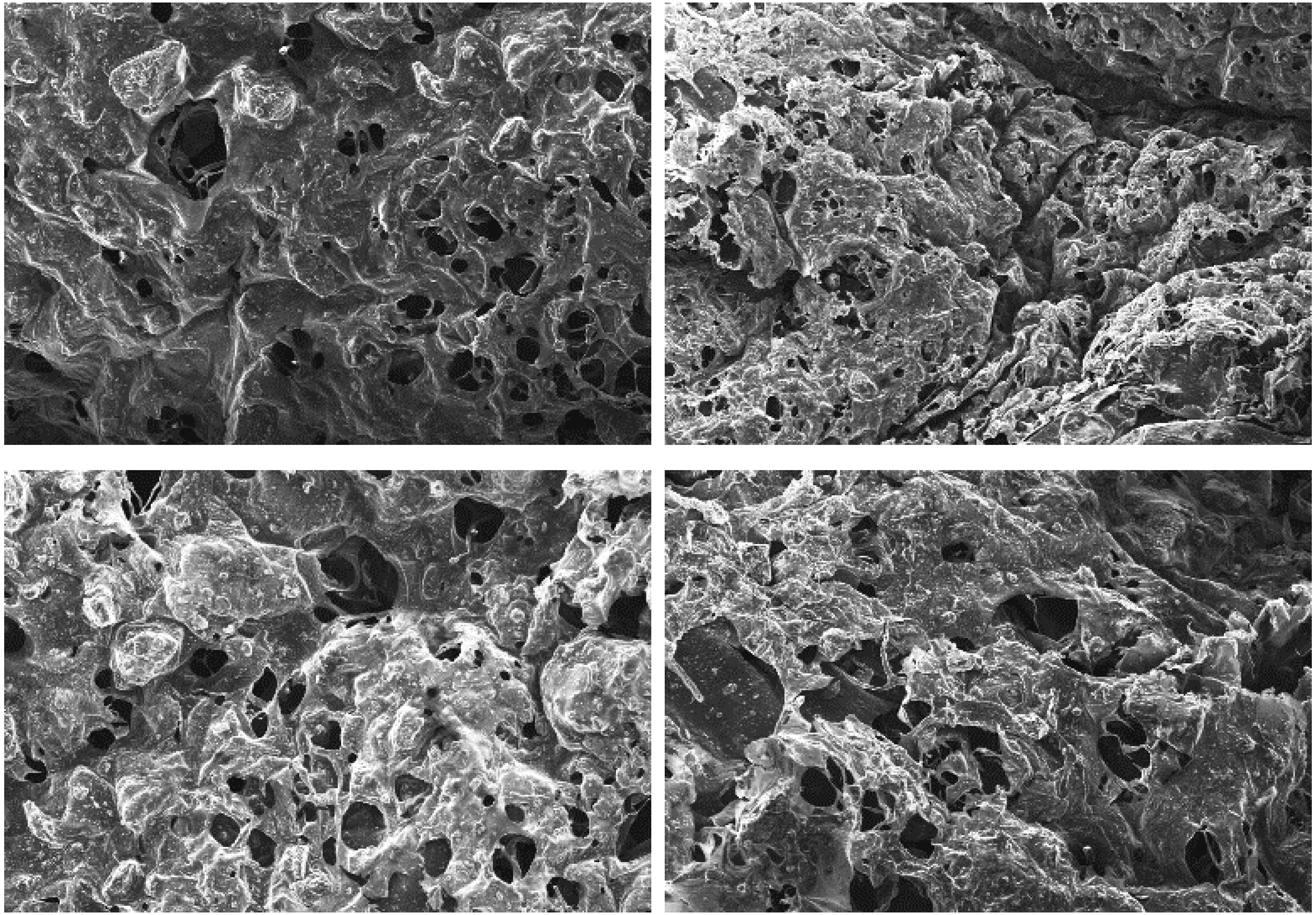
Aerogel preparation

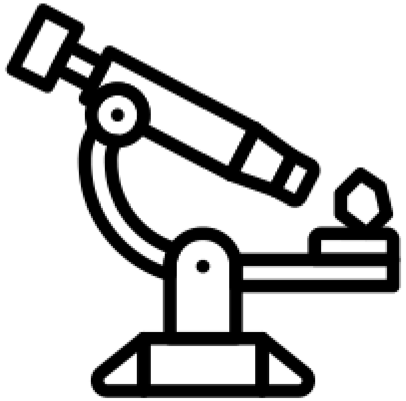


Preparation of aerogel: imine-bonded network generation.

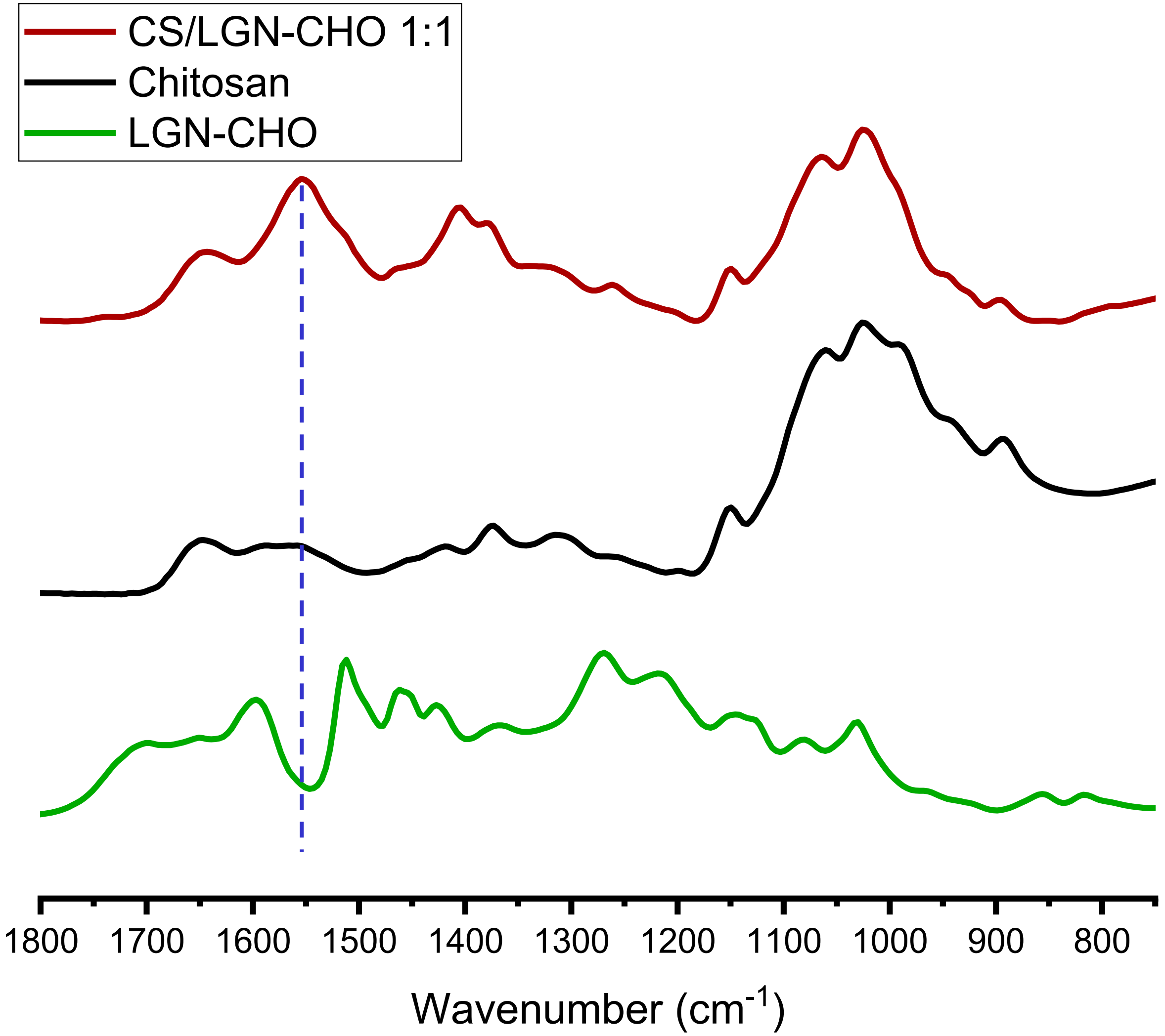
Aerogel characterization



Some SEM micrograph of the produced aerogel. We can see the microporous structure.

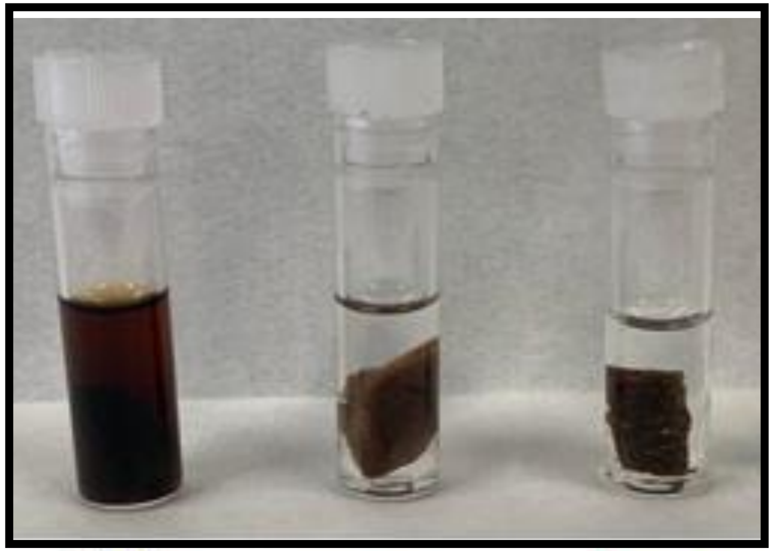


Aerogel characterization



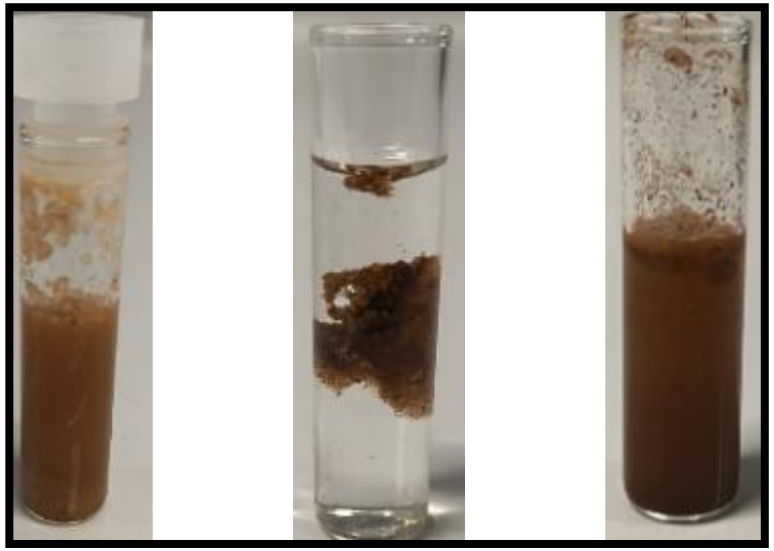
From FT-IR analysis we can recognise imino bond presence in the aerogel (1550 cm^{-1})

Aerogel stability



DMF water hexane

SOLVENTS



Acidic	Neutral	Basic
6<	7	>10

pH CONDITIONS

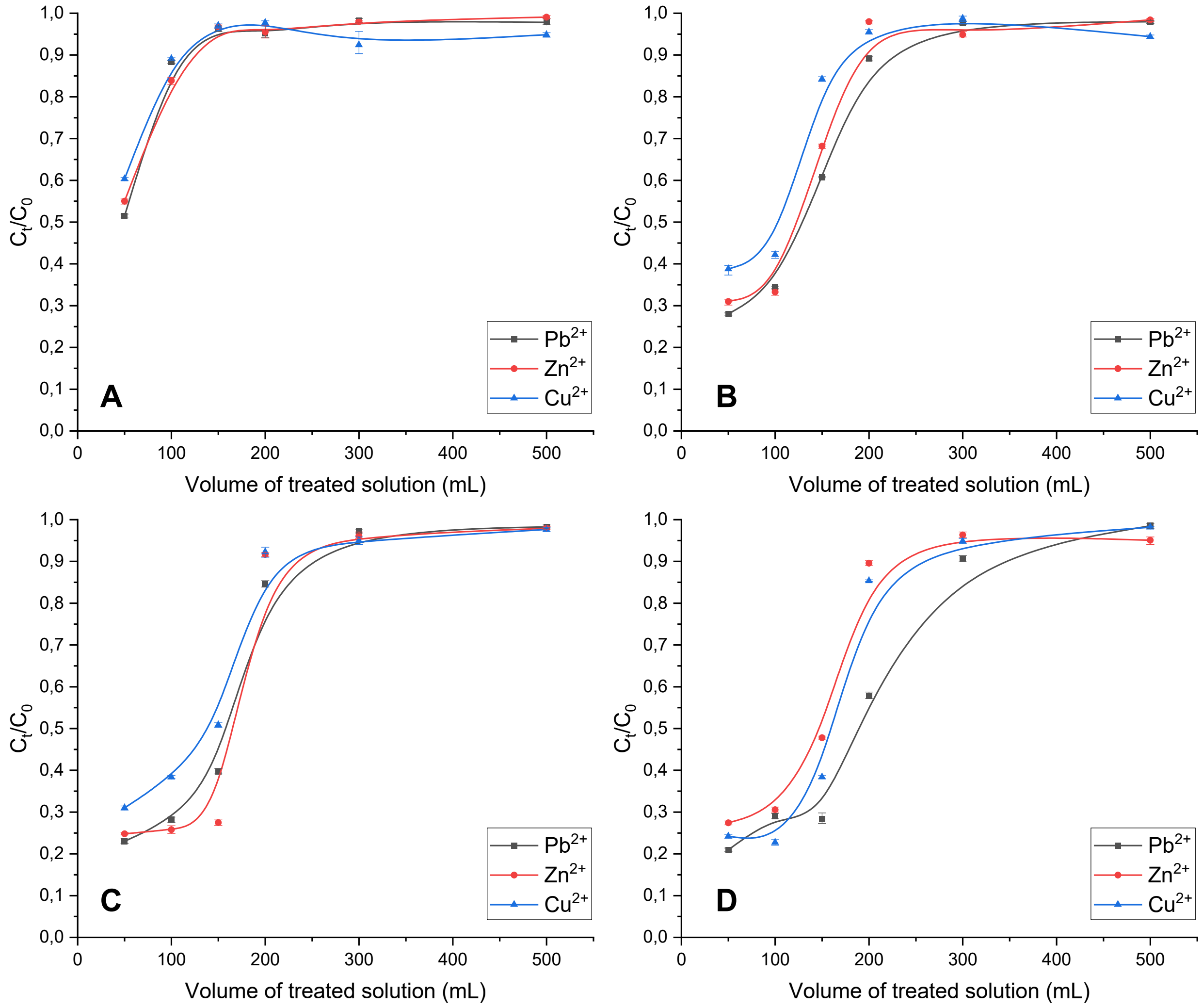
Dual-use: Water remediation

Sample	Metals		
	Pb^{2+} (mg g^{-1})	Zn^{2+} (mg g^{-1})	Cu^{2+} (mg g^{-1})
CS/LGN-CHO 1:1	28.8	27.7	31.1
CS/LGN-CHO 1.5:1	29.9	26.5	31.5
CS/LGN-CHO 2:1	30.2	26.9	32.8

Heavy metal adsorption (mg g-1) detected using aerogels as adsorbent

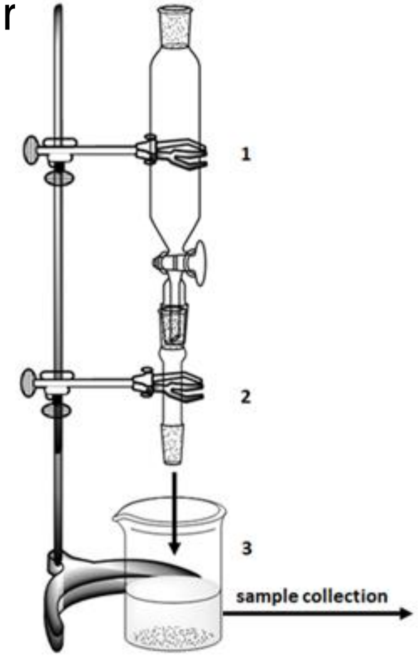
Batch absorption test: different aerogel performance

Dual-use: Water remediation



A CS; **B** CS/LGN-CHO aerogel 1:1; **C** CS/LGN-CHO aerogel 1.5:1; **D** CS/LGN-CHO aerogel 2:1. C_t = concentration of ions in the eluate, C_0 = concentration of ions in the untreated water (15 mg/L).

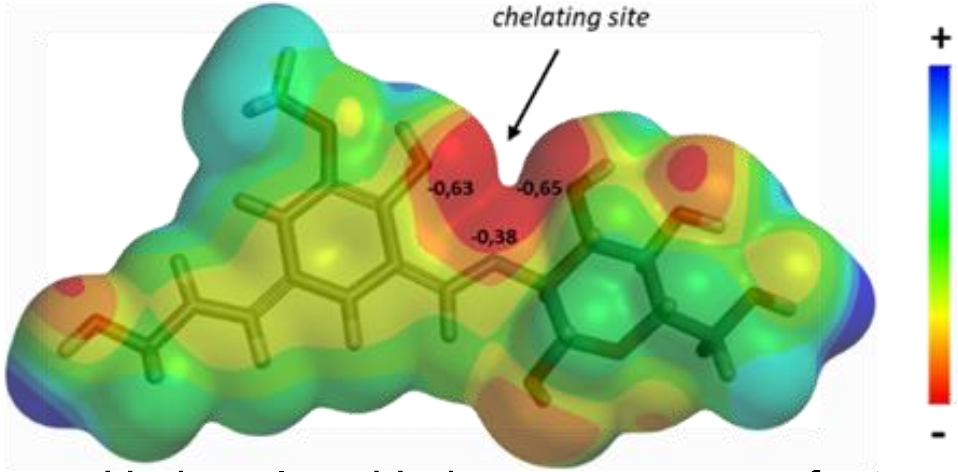
- **Efficiency** Ranking: CS/LGN-CHO 2:1 > 1.5:1 > 1:1 > Pure CS.
- **Operational Capacity**: Significant increase in breakthrough volume (Vb) attributed to the aerogel's porous architectur
- **Versatility**: Effective simultaneous removal of multiple metallic cations (Pb^{2+}, Zn^{2+}, Cu^{2+}) under dynamic flow conditions.



Experimental set-up

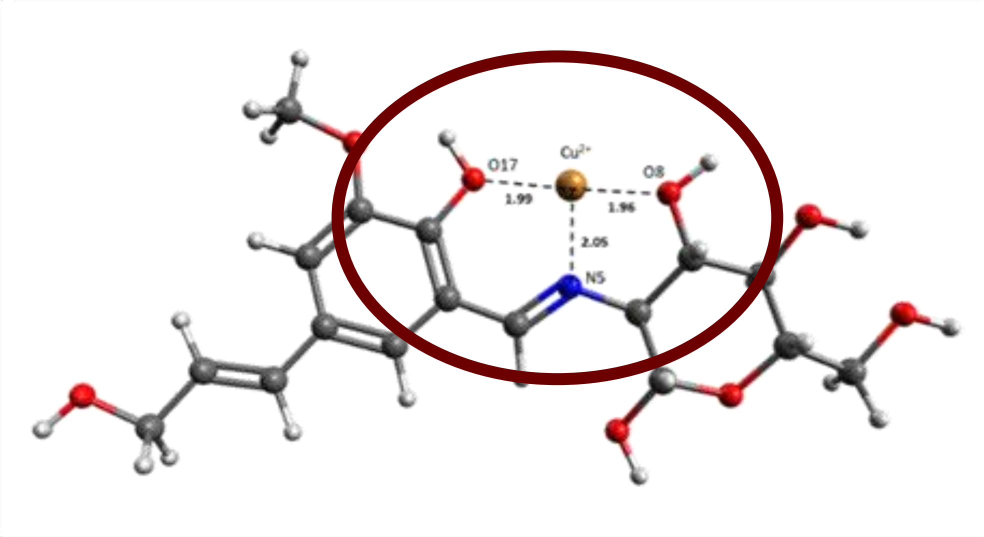
DFT calculation: ONO chelating site

a



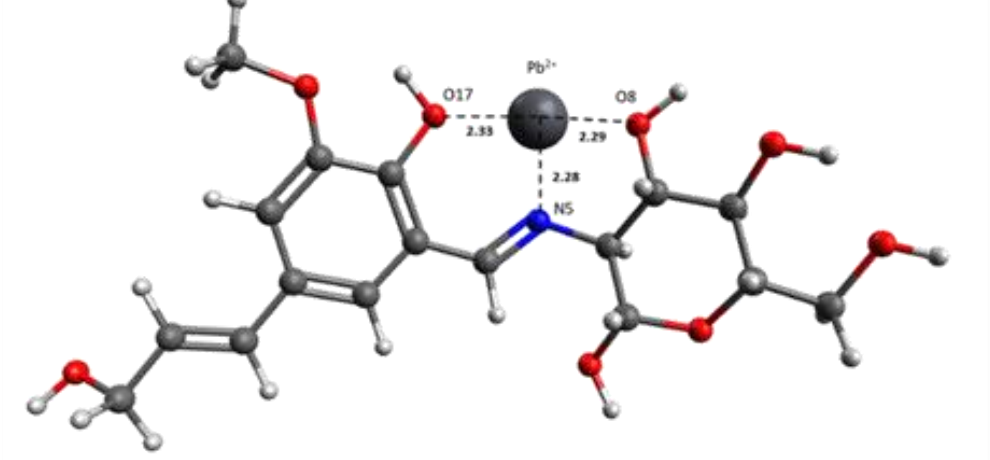
Hydroxyl and imino groups: a perfect chelating site for Heavy Metals

b



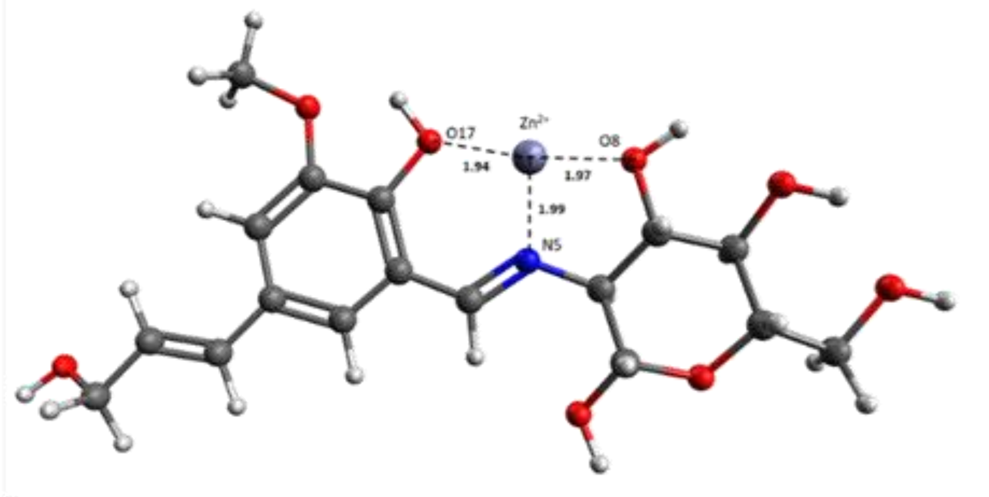
Chelating site: Copper

c



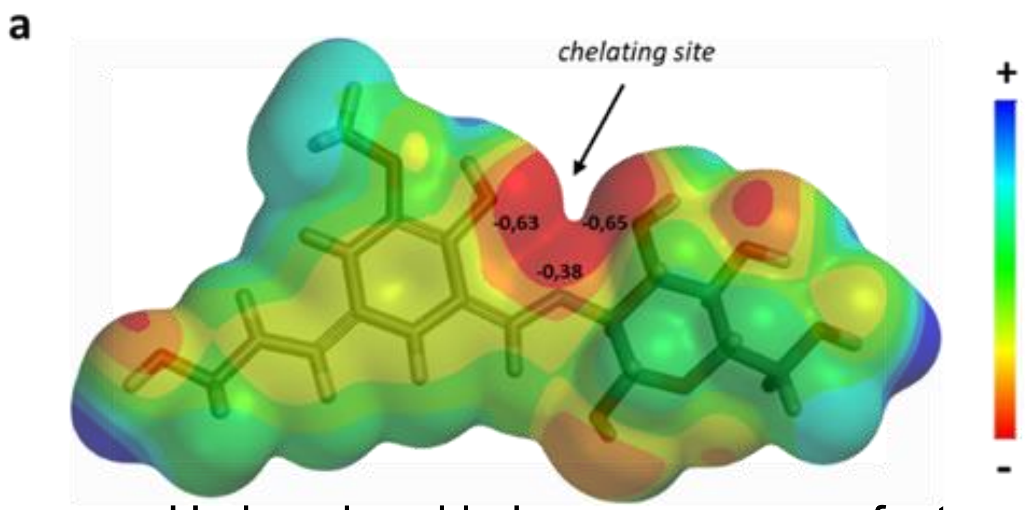
Chelating site: Lead

d

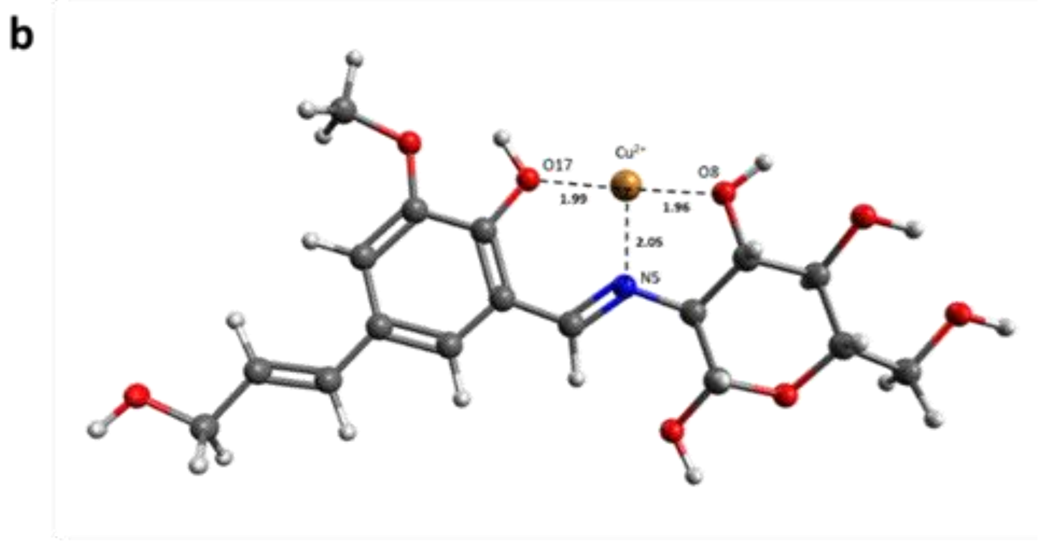


Chelating site: Zinc

DFT calculation: ONO chelating site



Hydroxyl and imino groups: a perfect chelating site for Heavy Metals



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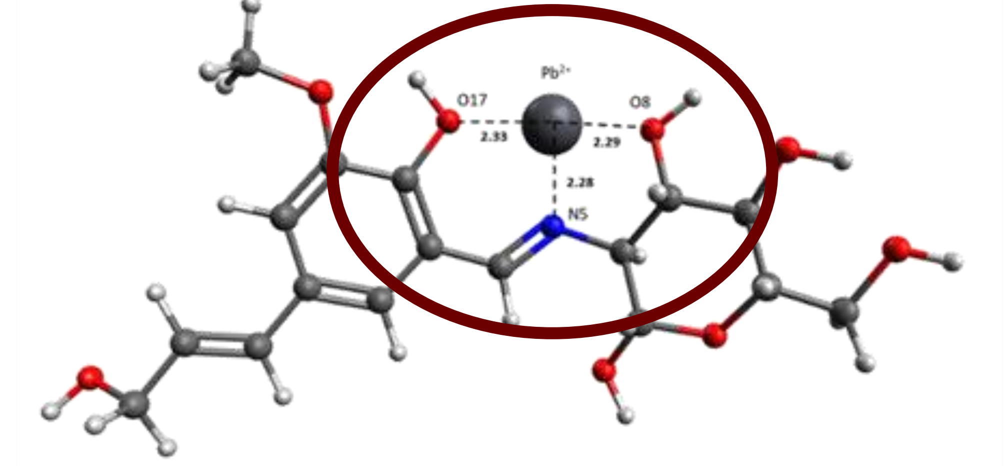

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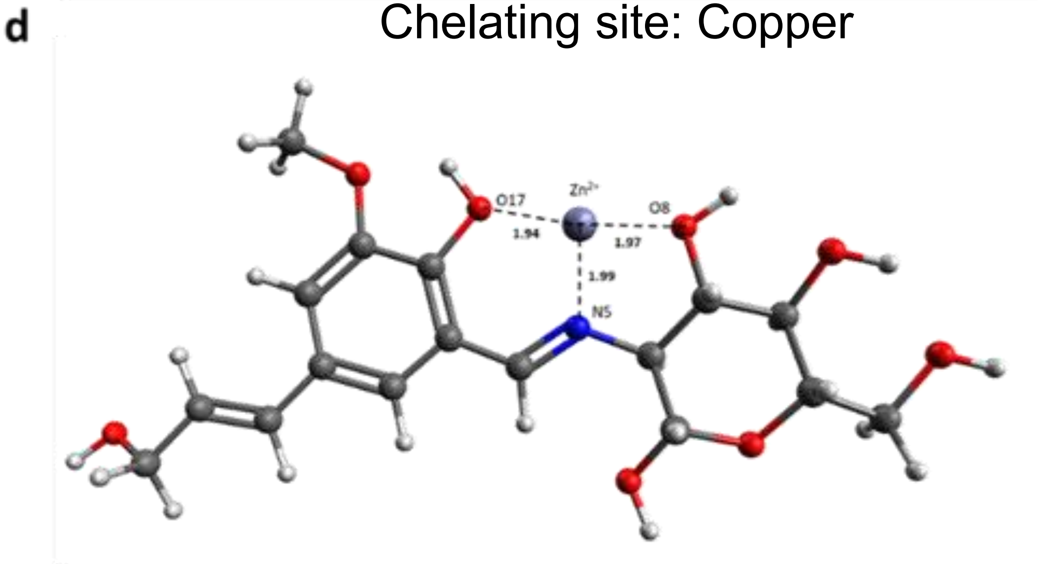

Chelating site: Zinc

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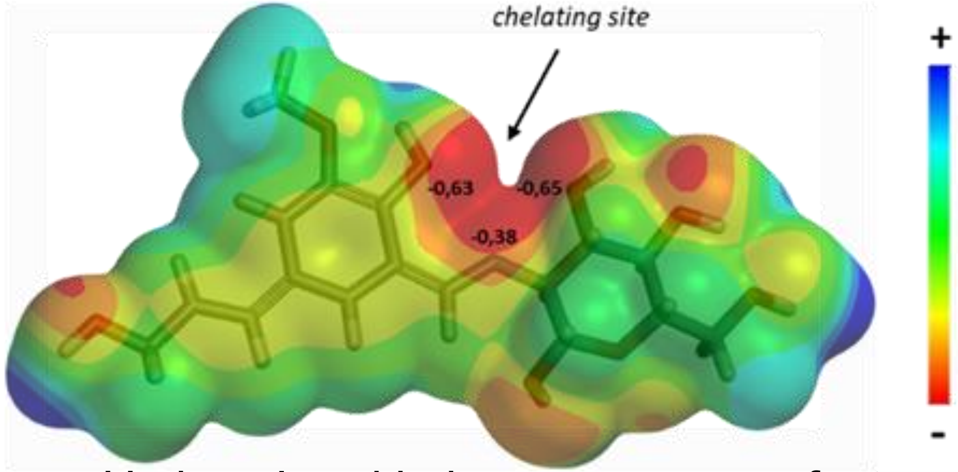

Hydroxyl and imino groups: a perfect chelating site for Heavy Metals

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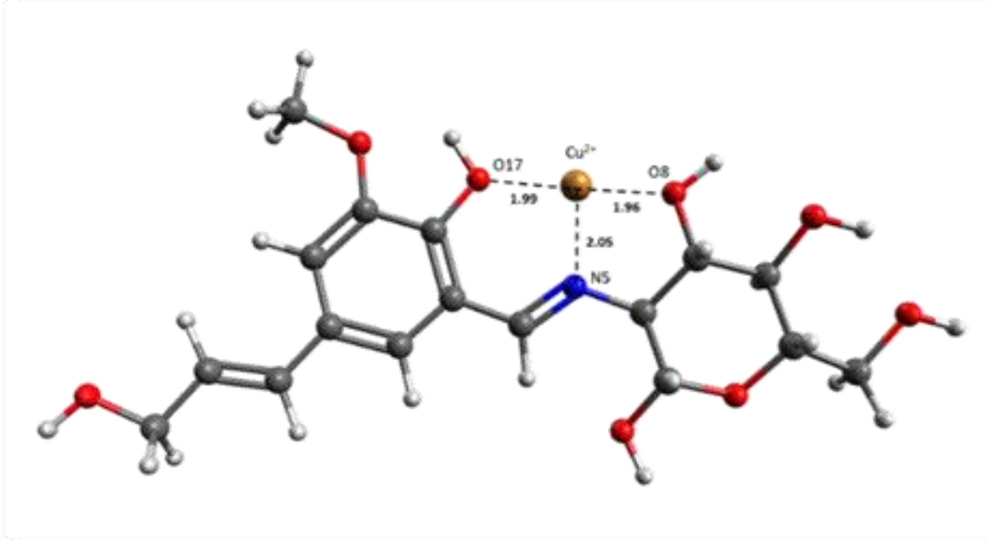
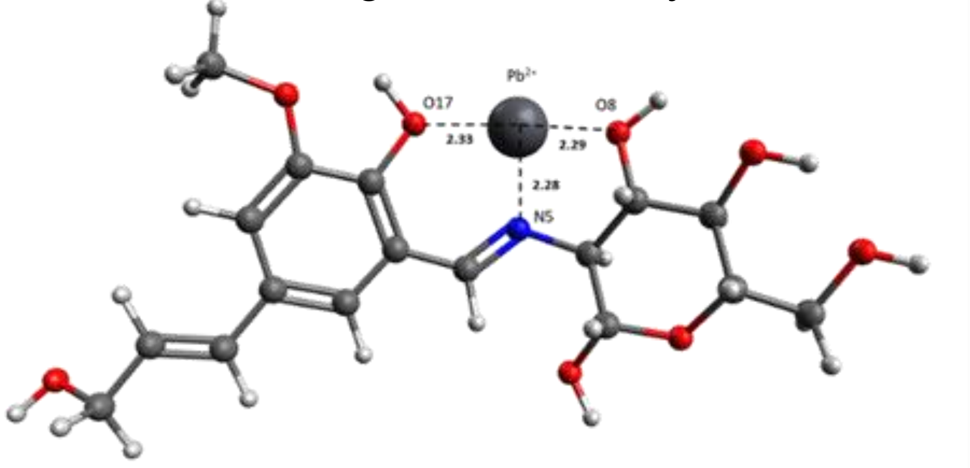


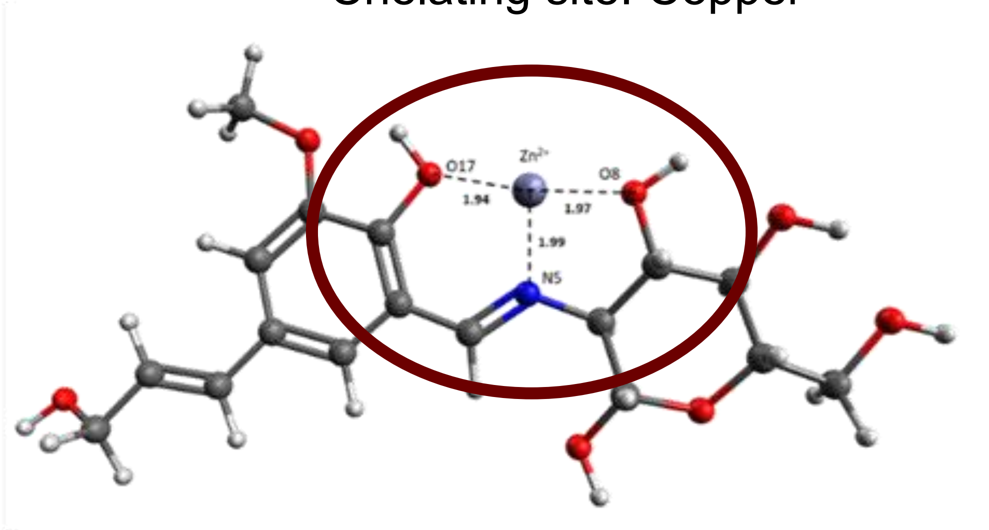
Chelating site: Copper

c



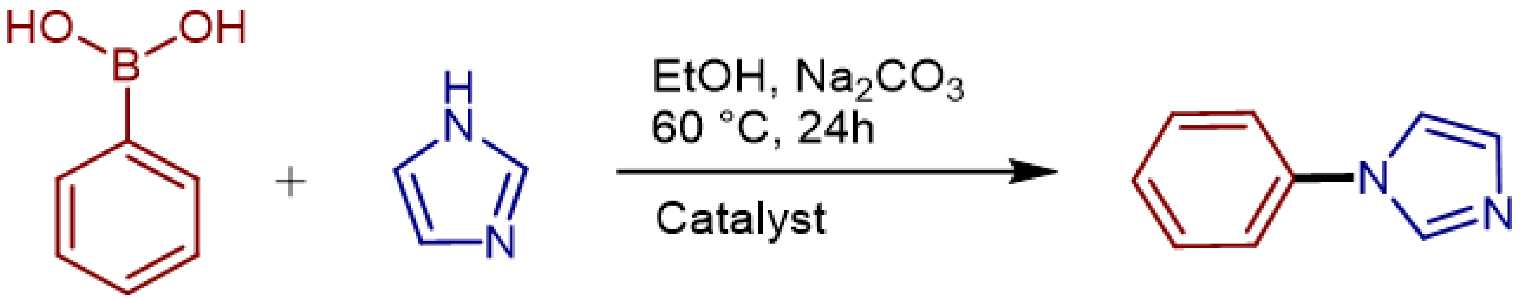
Chelating site: Lead

d



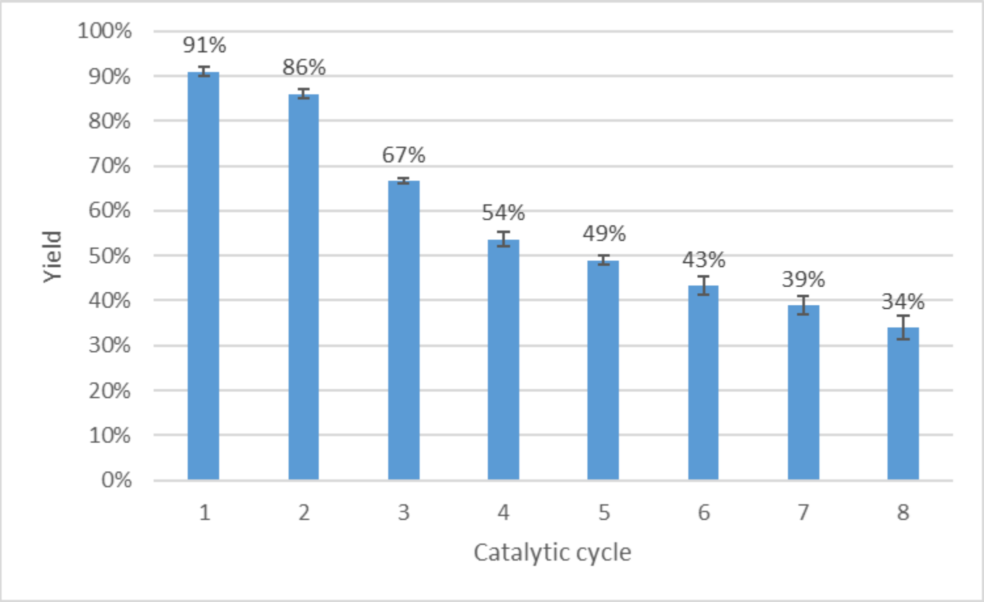
Chelating site: Zinc

Dual-use: Catalysis



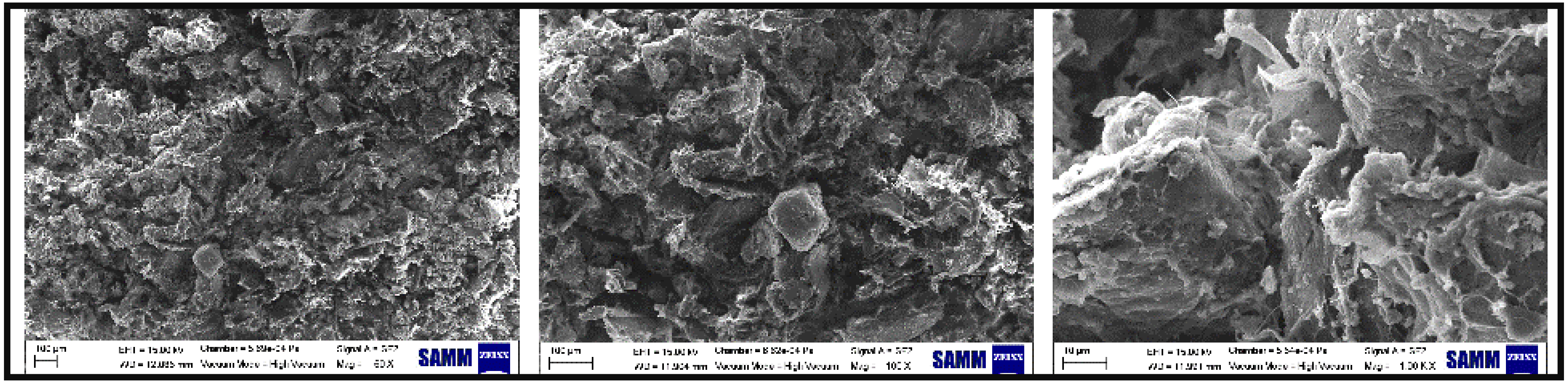
Proof-of-concept:

Chan-Lam cross coupling reaction.

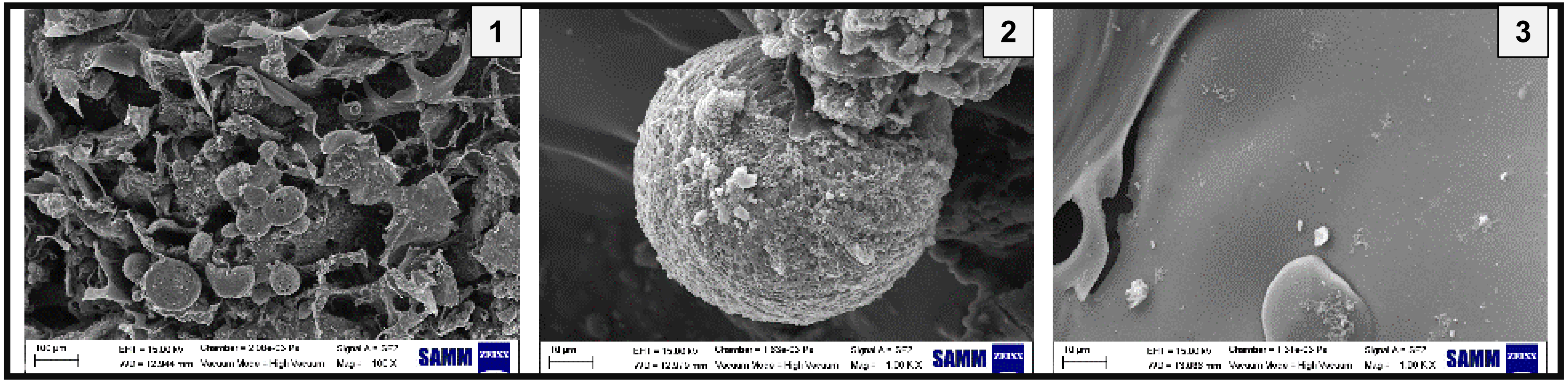


Catalytic activity of the Cu-impregnated aerogel.

Dual-use: Catalysis

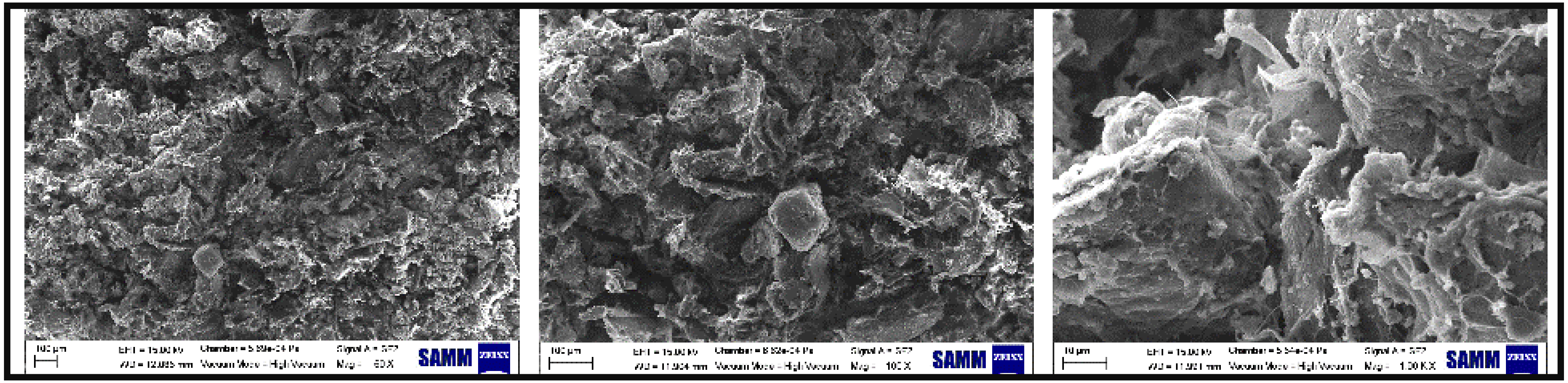


SEM micrographs of impregnated Aerogel before the **first** catalytic cycle.

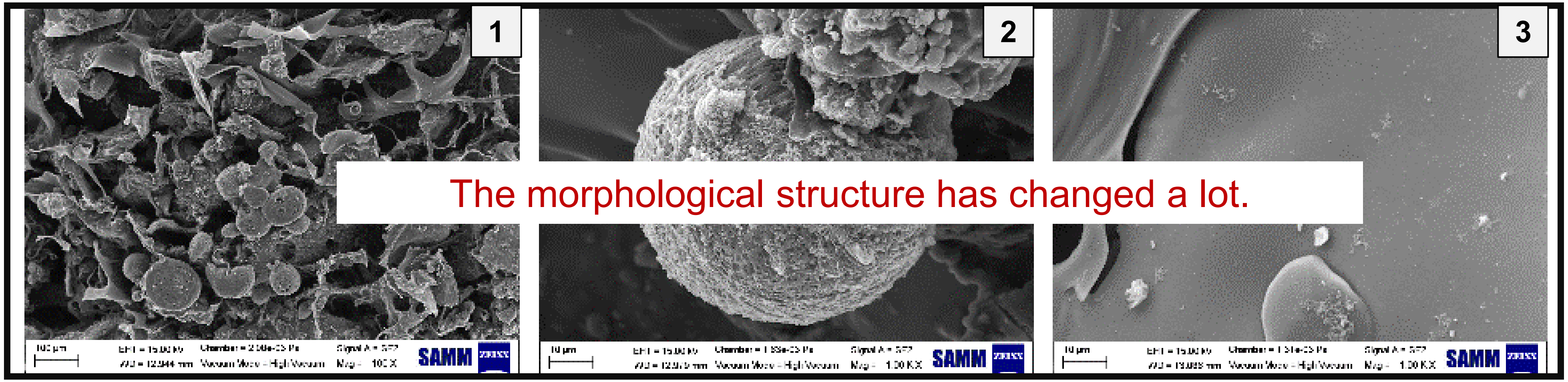


SEM micrographs of impregnated Aerogel after the **eight** catalytic cycle.

Dual-use: Catalysis



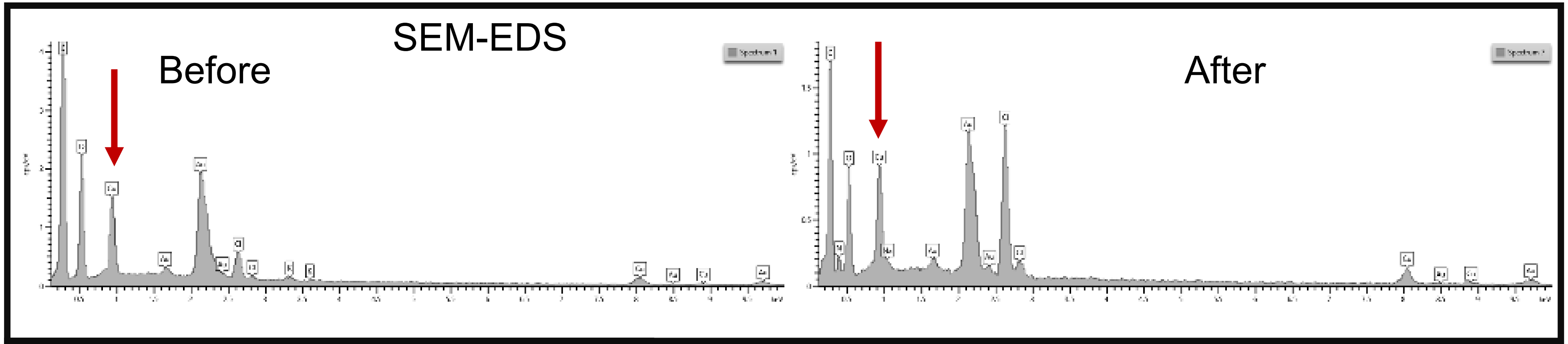
SEM micrographs of impregnated Aerogel before the **first** catalytic cycle.

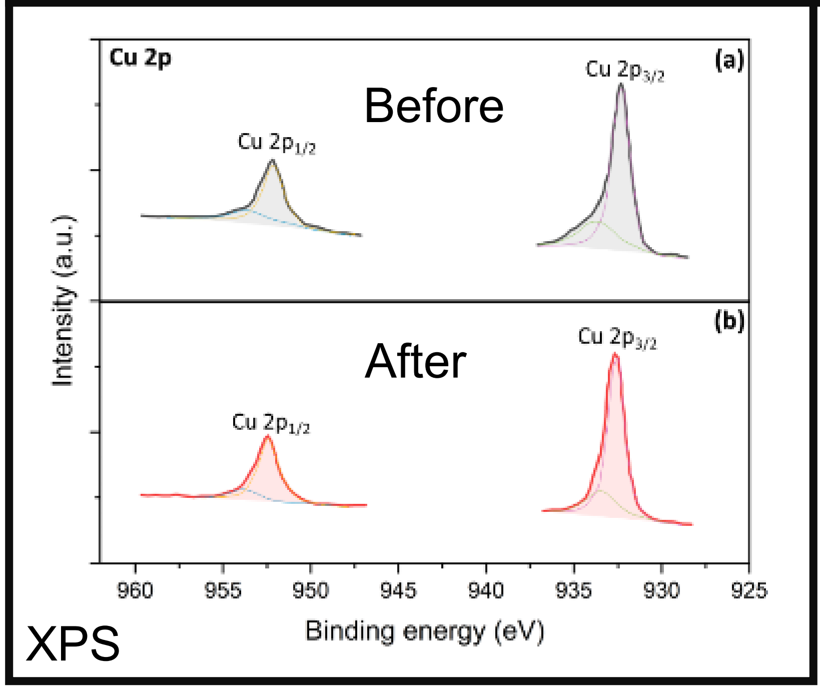


The morphological structure has changed a lot.

SEM micrographs of impregnated Aerogel after the **eight** catalytic cycle.

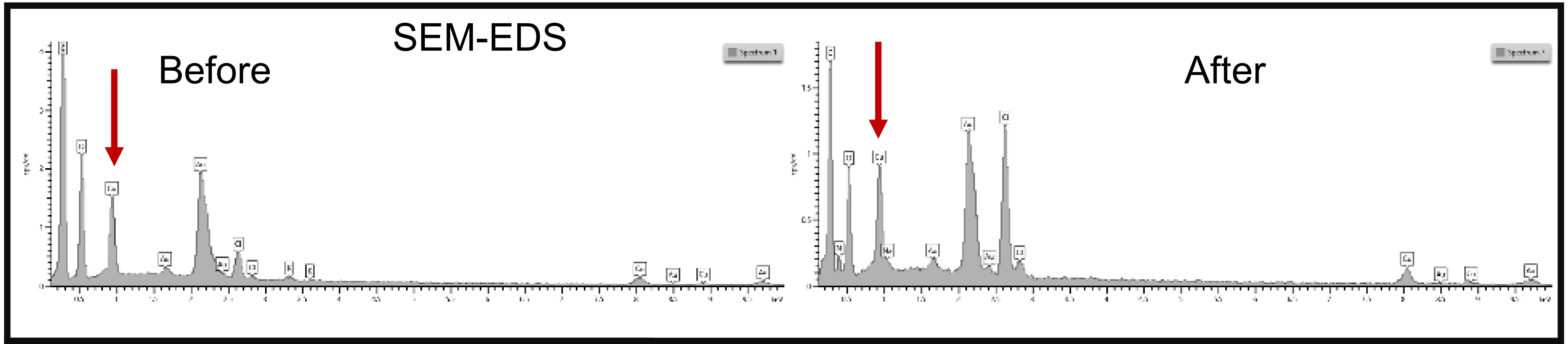
Dual-use: Catalysis

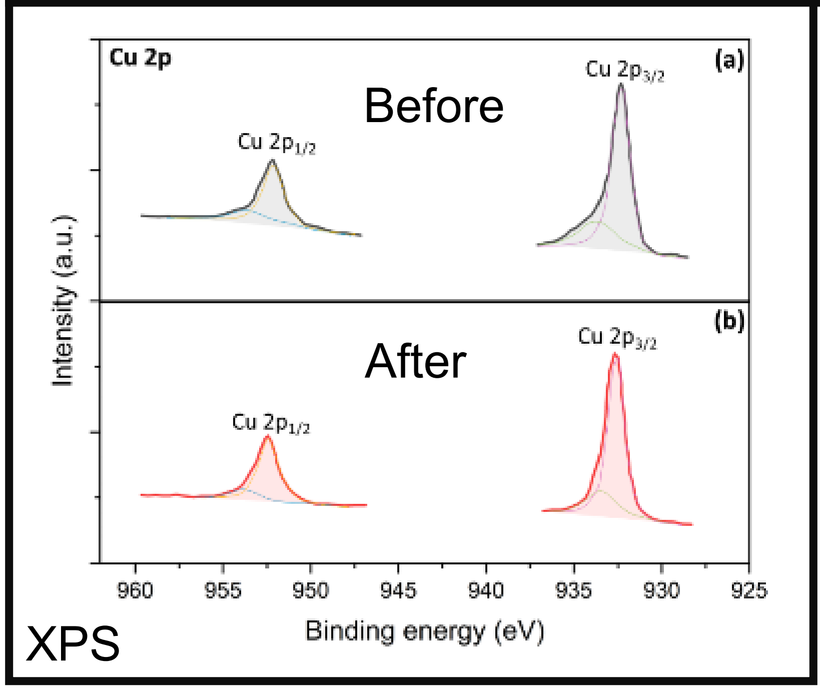




SEM-EDS and XPS analysis shows no change in Cu content and oxidation state.

Dual-use: Catalysis





SEM-EDS and XPS analysis shows no change in Cu content and oxidation state.

The decrease of catalytic activity is due to microstructure **degradation** and no leak or oxidation of copper is observed.

Close the loop: Aerogel regeneration

Native aerogel 1:1 CS/LGN-CHO

↓

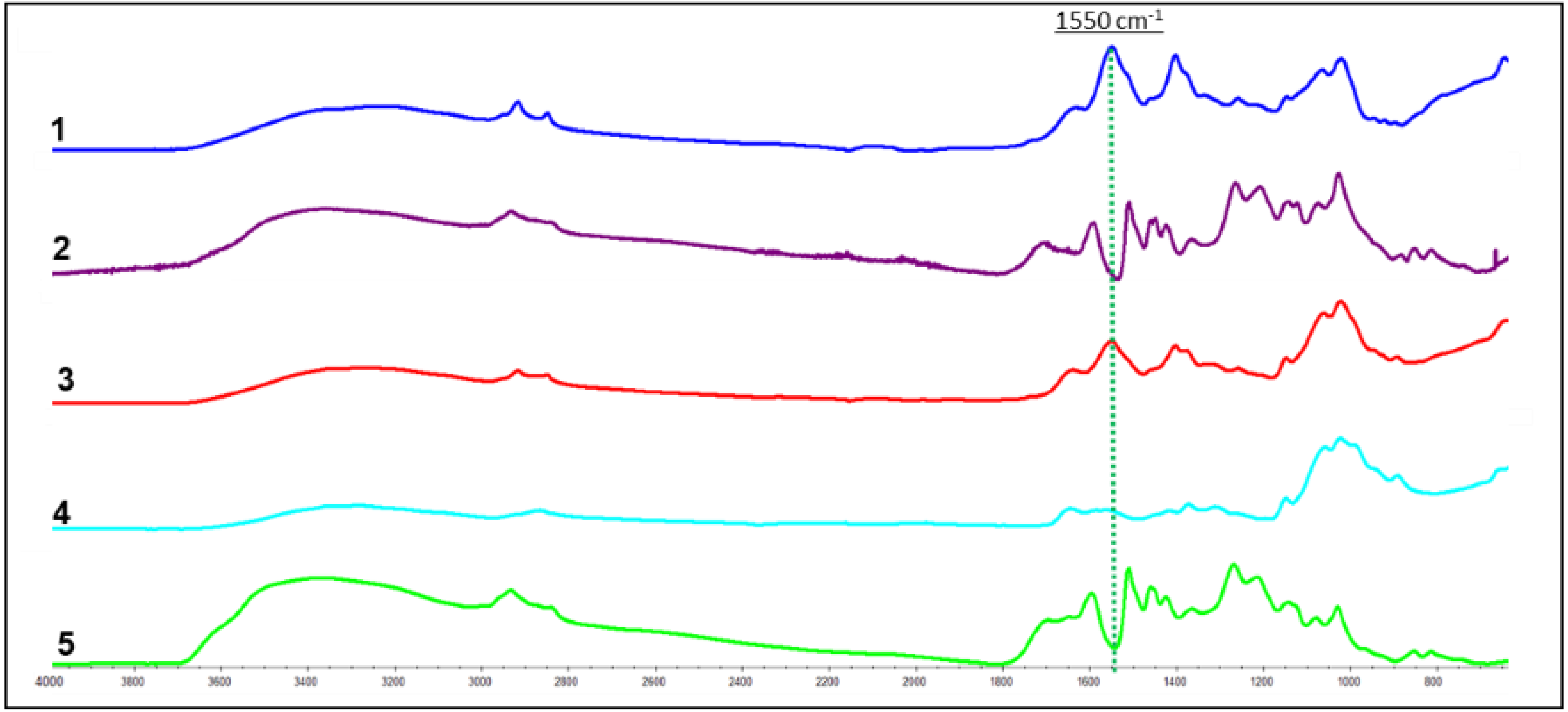
Dissolution of aerogel: pH 4, 30 days

↓

pH 7 Freeze drying: regenerated aerogel

↓

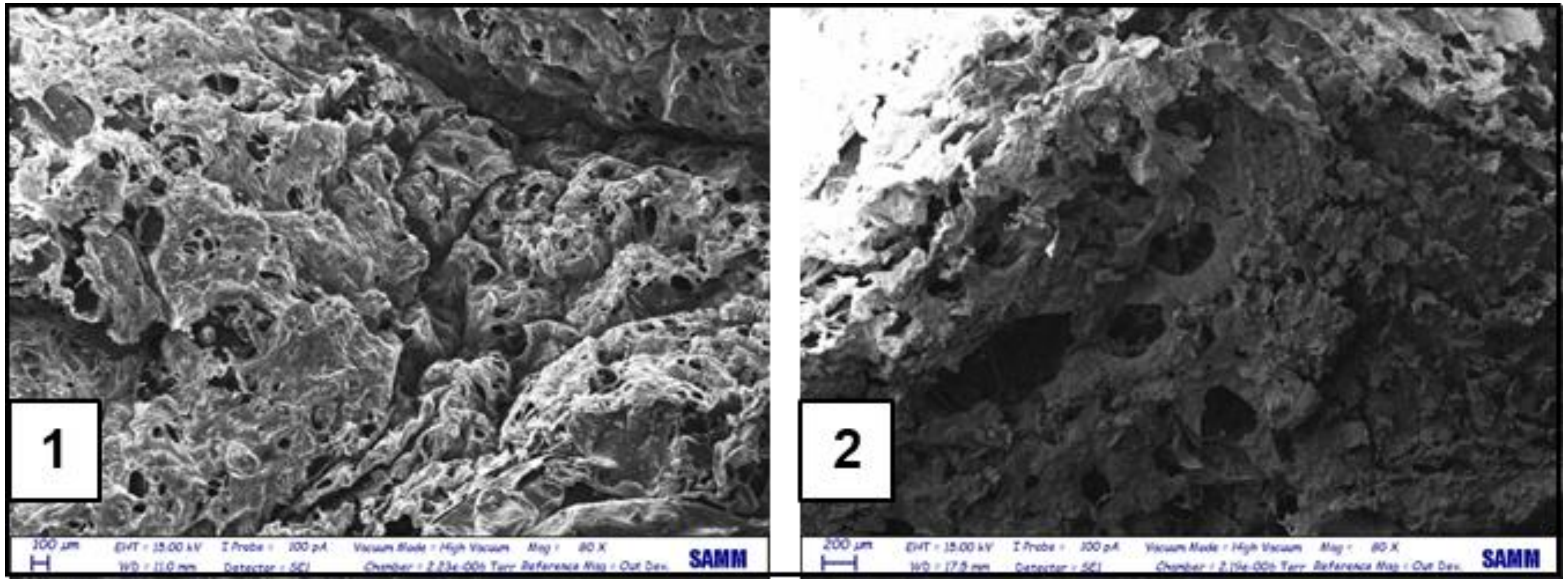
Chan-Lam catalysis to test regenerated aerogel



FT-IR spectra of the acid-treated aerogel CS/LGN-CHO 1:1.

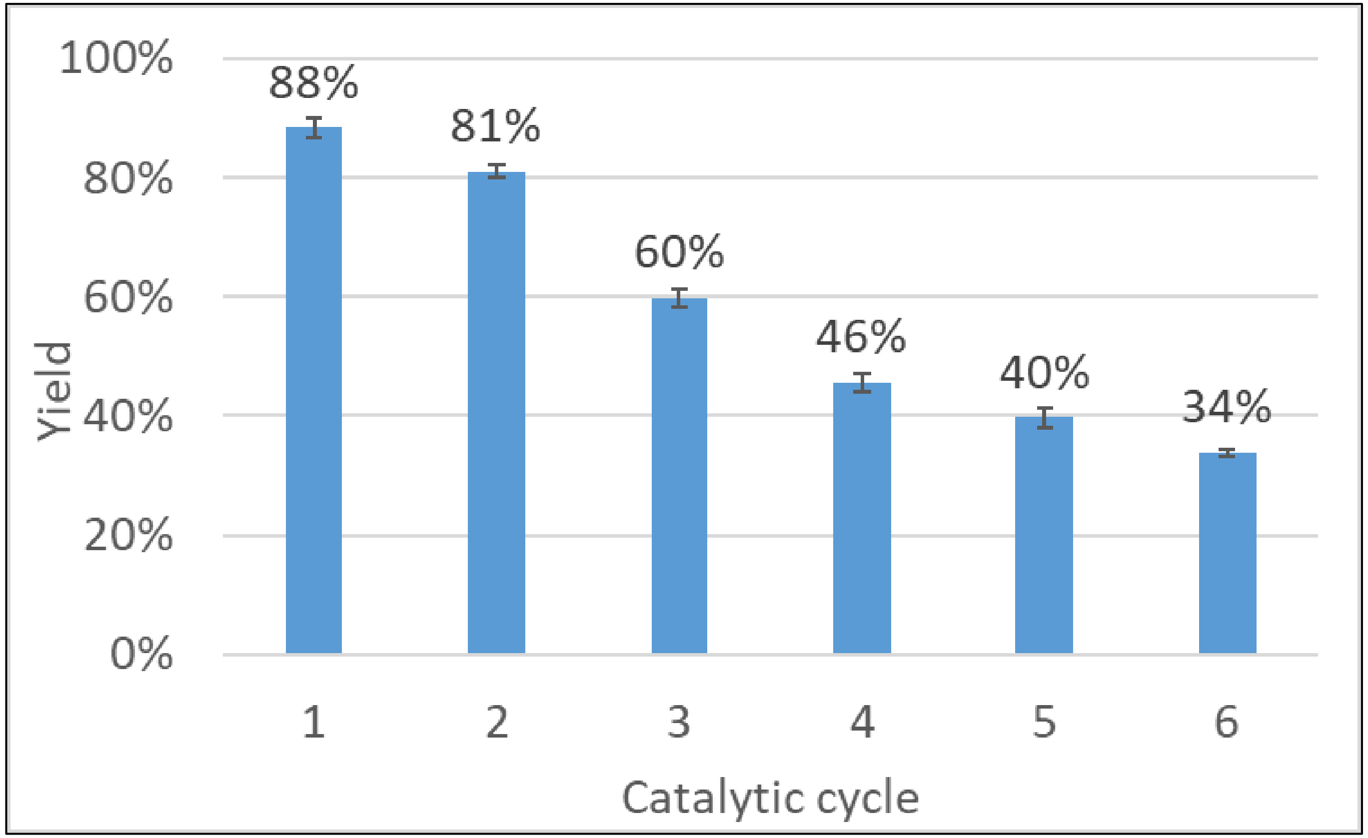
1. Regenerated aerogel.
2. Treated aerogel (pH 4, 30 days).
3. Untreated aerogel.
4. Chitosan.
5. Formylated Lignin.

Close the loop: Aerogel regeneration

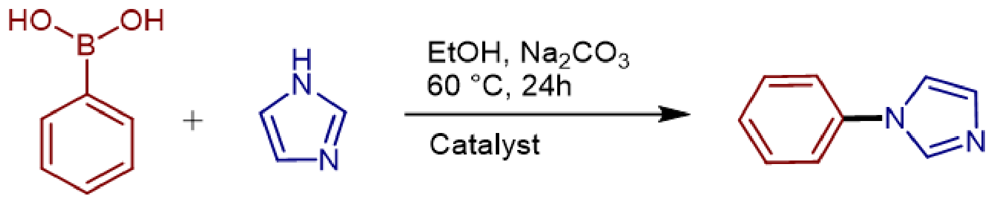


SEM micrograph of: untreated aerogel (1); regenerated aerogel (2);

Close the loop: Aerogel regeneration

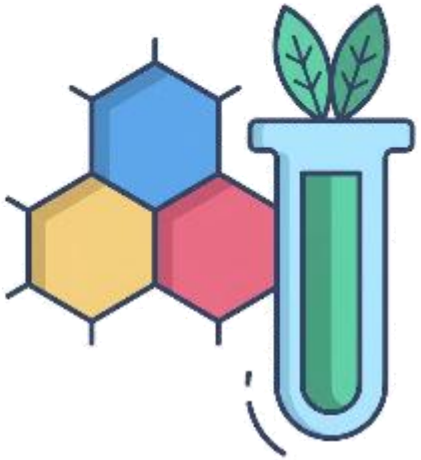


Catalytic performances of the **regenerated** aerogel.



Proof-of-concept:

Chan-Lam cross coupling reaction.



In conclusion

Take home messages:

- A bio-based platform has been prepared
- Dual use: water remediation and catalysis
- Regenrability and reuse: ctatalysis proof of concept

For the future

Nex steps:

- Scaling up production
- Strength test on others synthesis
- Other heavy metals filtration

Thanks to….

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ISMaterials group:

Prof Maurizio Galimberti

Prof Vincenzina Barbera

Dr Davide Gentile

And all of the students

Thanks to….

Innovative Sustainable Materials Group

ISMaterials group

Thanks

for your attention!