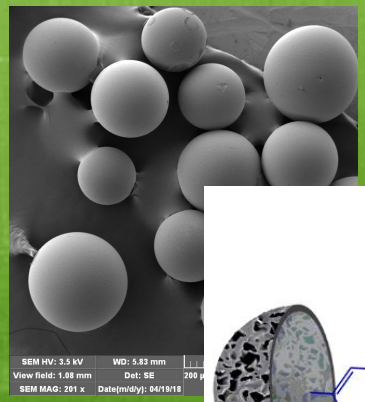
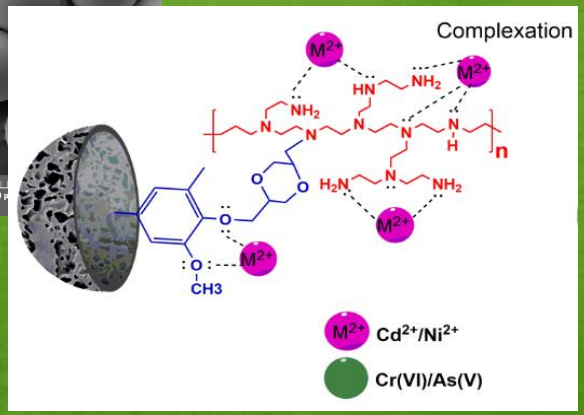




October 23, 2020

Lignin microspheres - a novel eco-friendly adsorption material

Ana Popović

PhD Candidate, University of Belgrade, Serbia, Faculty of Technology and Metallurgy

Introduction: Why lignin?

- **waste by-product** from the pulp and paper industry or biomass pretreatment processes
- **underexploited**
- possibility of **valorization**
- second generation biomass
- substance with a **binding** properties that causes the **compactness** of wood cell structure
- **abundant**, low-in cost, and **eco-friendly**

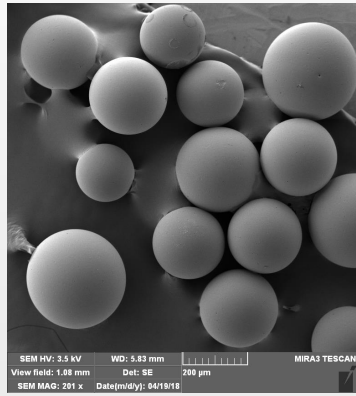
- **kraft lignin** was used in our research

Lignin-based microspheres

- The presence of various **functional groups** (aliphatic and aromatic/phenolic OH - groups) makes lignin a suitable substance for chemical syntheses to form **polymer materials**

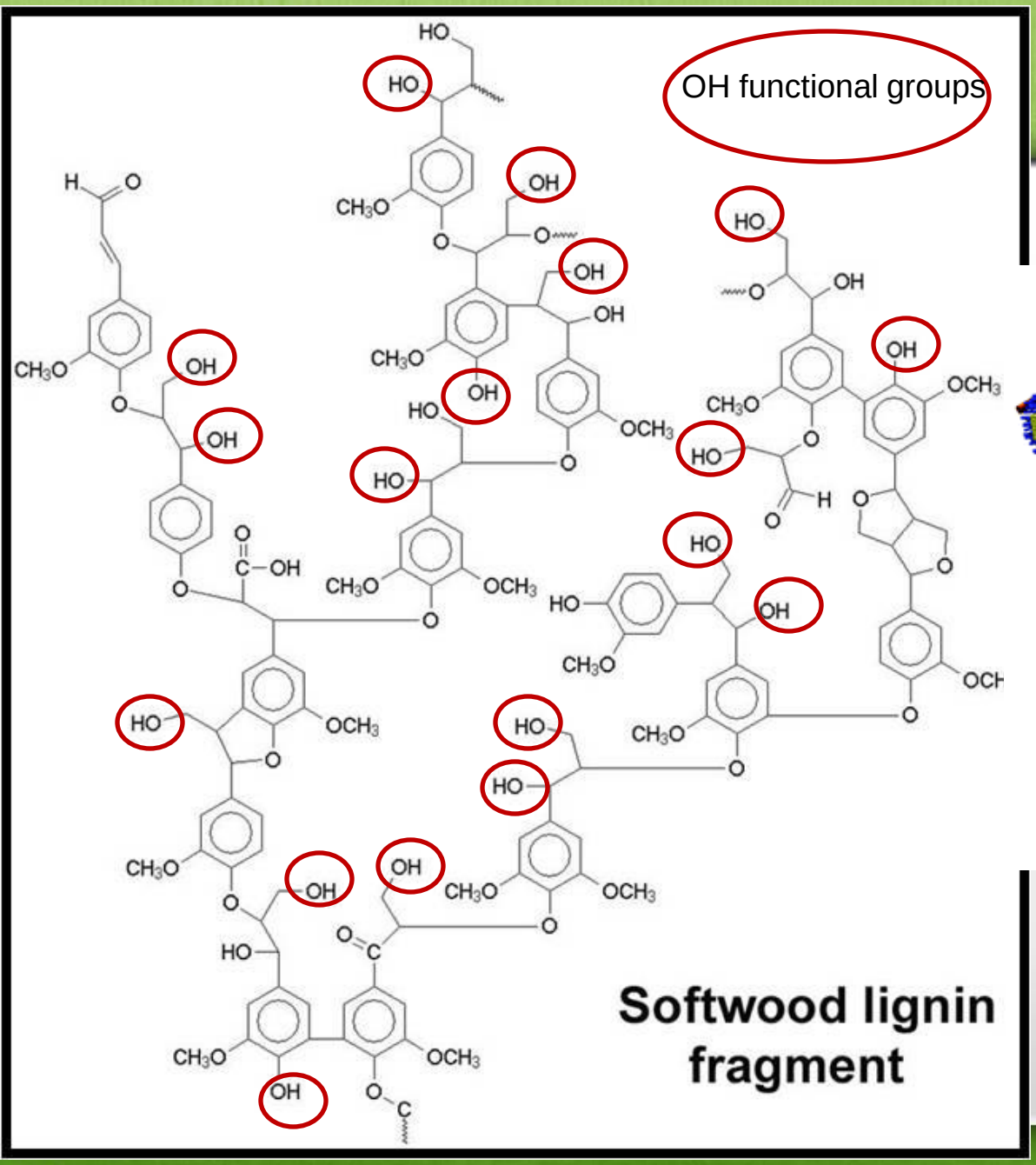
Our research product:

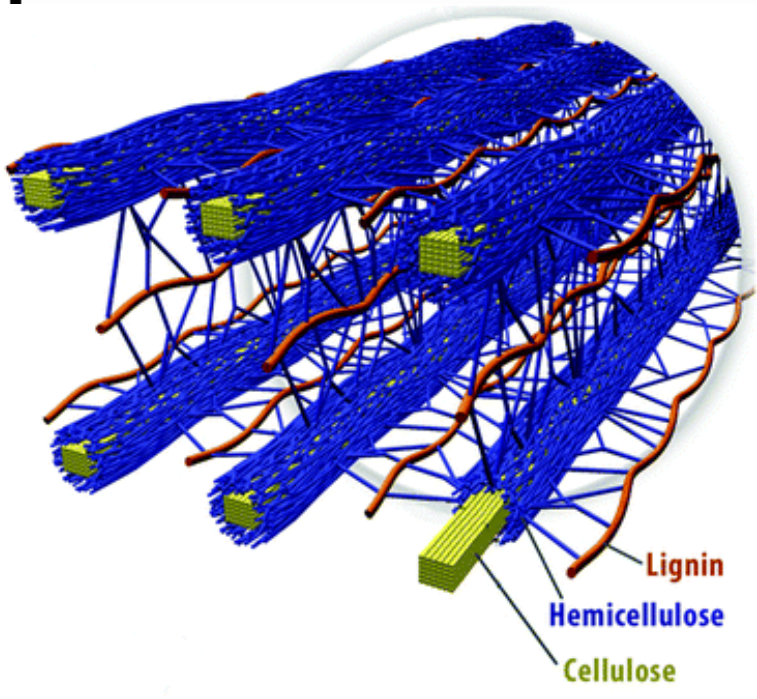
- **Lignin microspheres** (**LMS**): An effective and recyclable natural polymer-based **adsorbent** for **diclofenac** and **heavy-metal ion** removal



2 methods of synthesis of LMS we used:

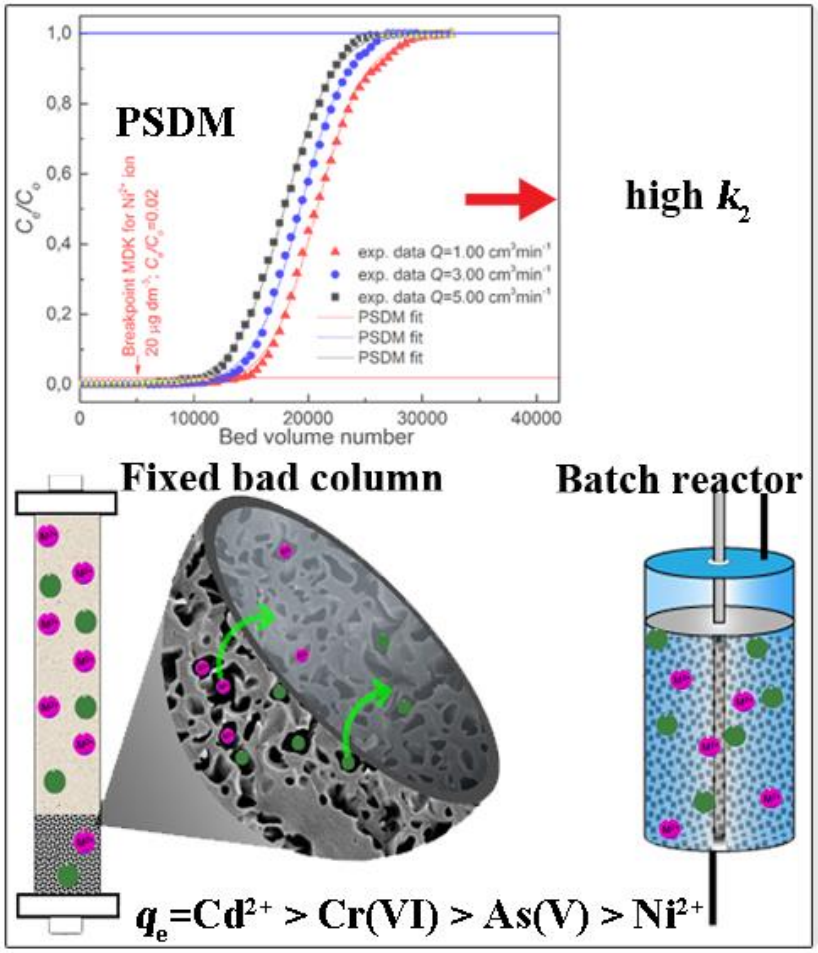
- inverse suspension copolymerization of lignin
- copolymerization of lignin methacrylic derivates prepared with methacryloyl chloride

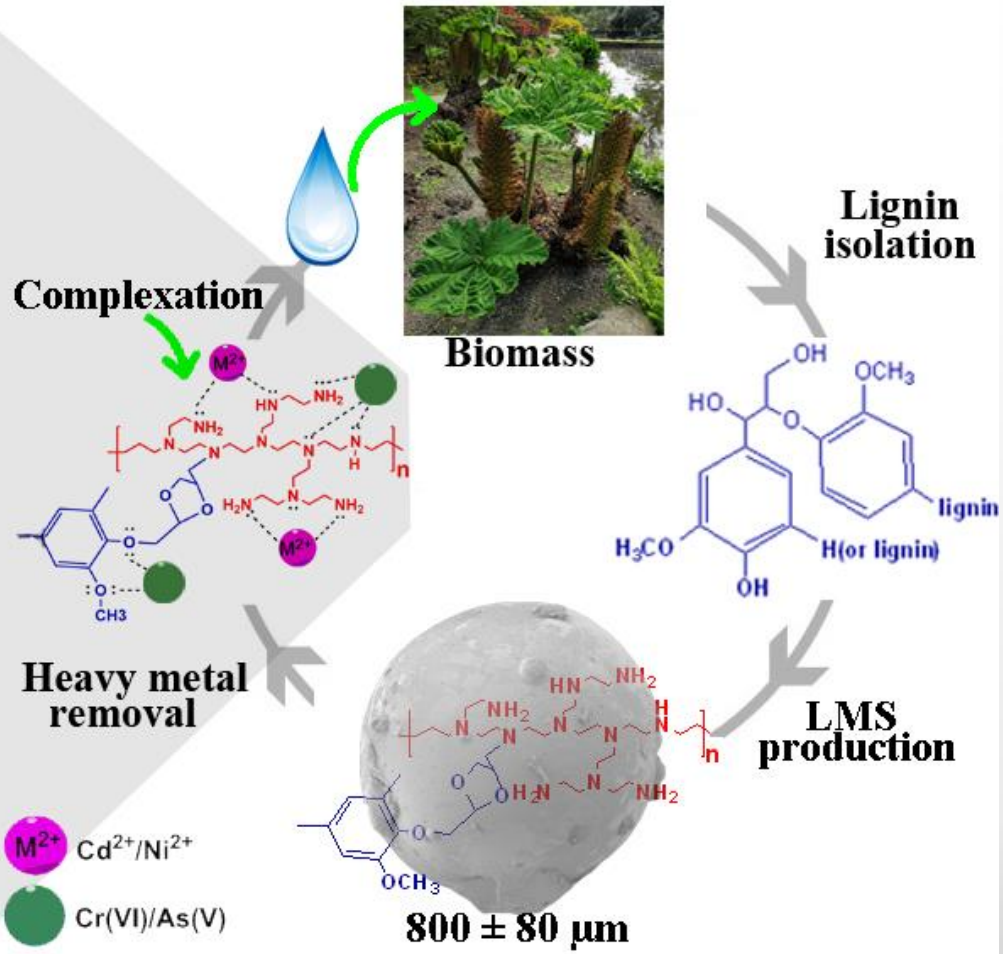




Ge et al. 2017

Summary of our research





Results

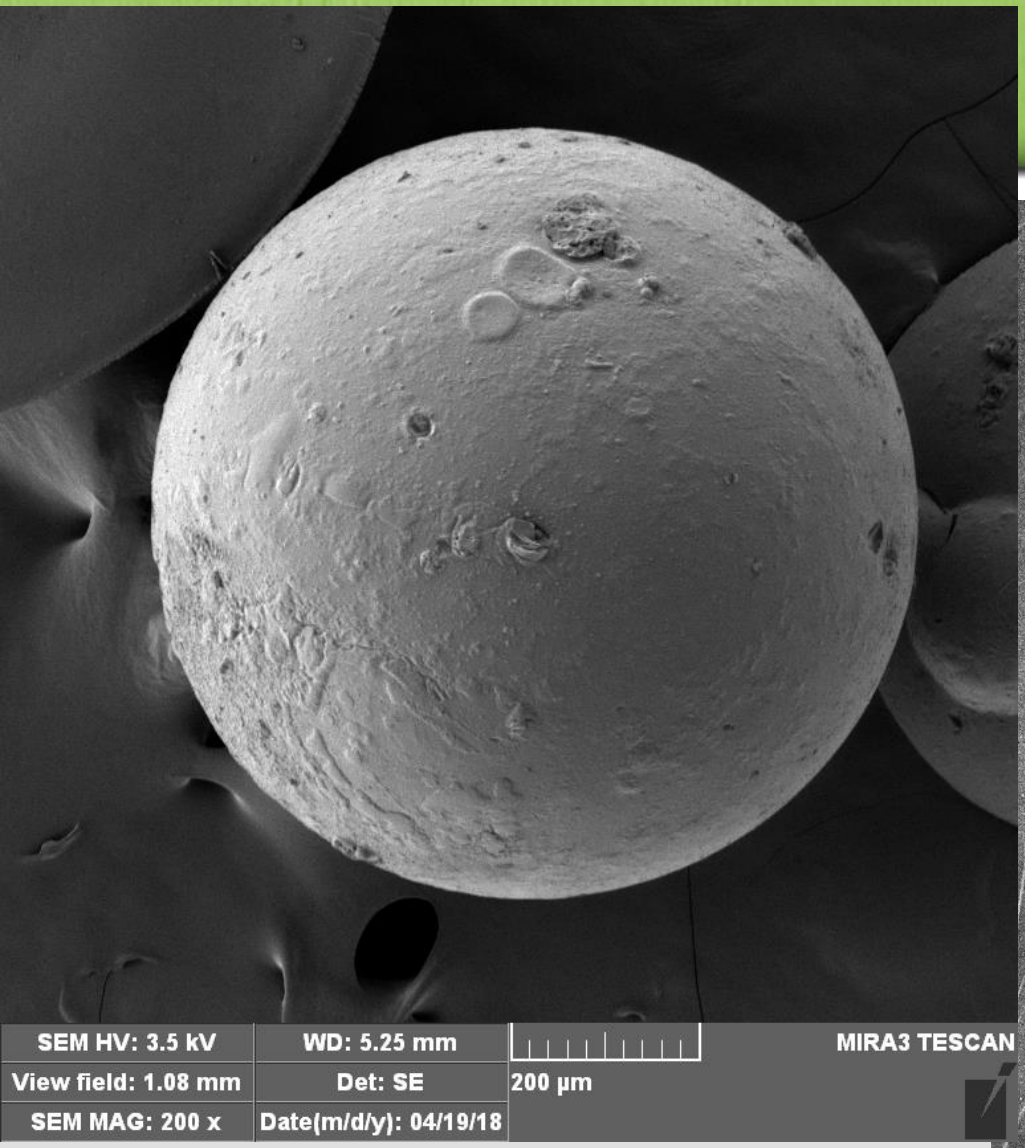
- **1 (LMS-1%):** LMS, with 1.0 wt.% Na-alginate solution
- **2 (LMS-5%):** LMS, with 5.0 wt.% Na-alginate solution
- **3 (LMS-10%):** LMS, with 10.0 wt.% Na-alginate solution
- **4 (LMS-Fe_3O_4):** LMS, with amino-modified Fe_3O_4 nanoparticles
- **5 (LMS-MnO_2):** LMS, with amino-modified MnO_2 nanoparticles
- **6 (L-MAC-MS-TMPTA):** Lignin methacrylic deriv. MS, TMPTA*
- **7 (L-MAC-MS-TEGDMA):** Lignin methacrylic deriv.MS, TEGDMA*
- **8 (L-MAC-MS-$_{MEMO}Fe_3O_4$):** LMS with MEMO* modified Fe_3O_4
- **9 (L-MAC-MS-$_{MAC}Fe_3O_4$):** LMS with methacrylic modified Fe_3O_4
- **10 (L-MAC-MS-$_{MAC}MnO_2$):** LMS with methacrylic modified MnO_2

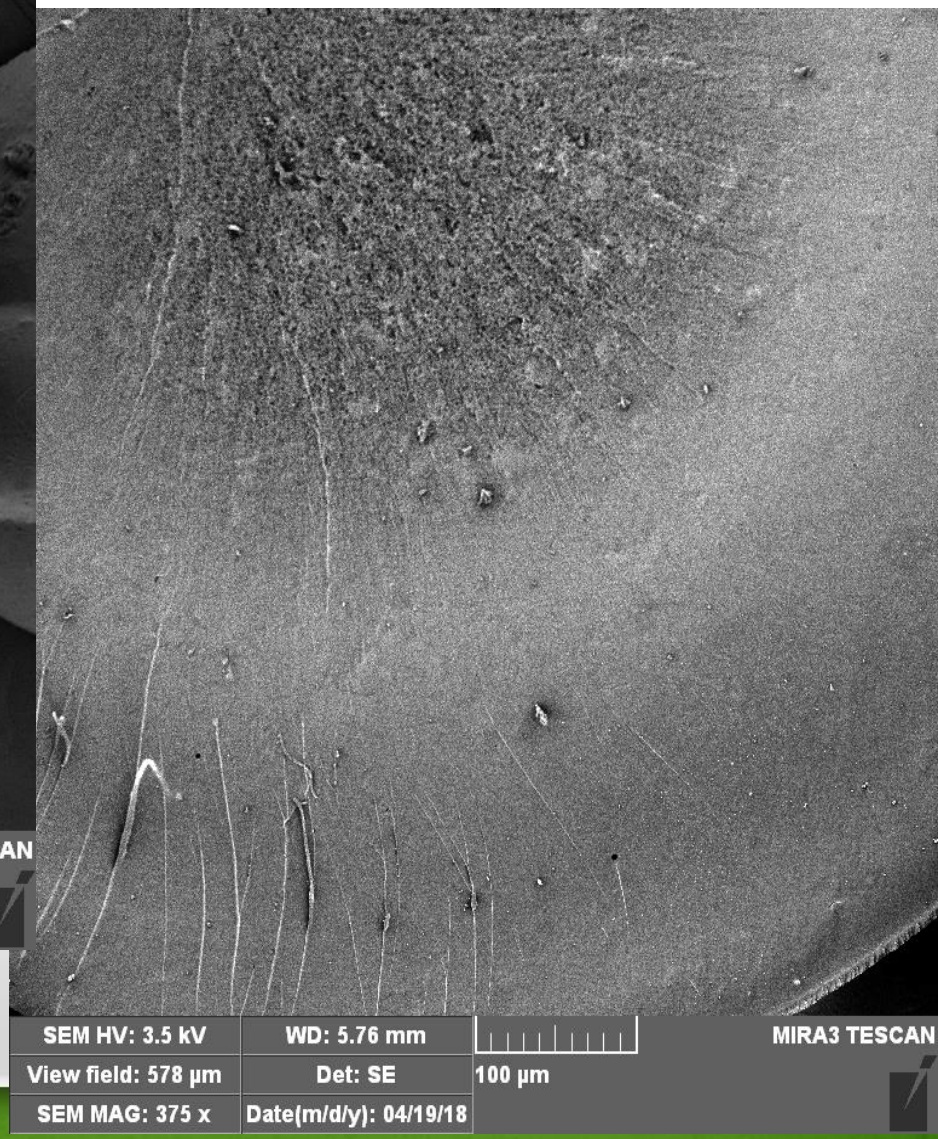
* Trimethylolpropane triacrylate; * Triethylene glycol dimethacrylate; * Methacrylfunctional silane

Characterisation

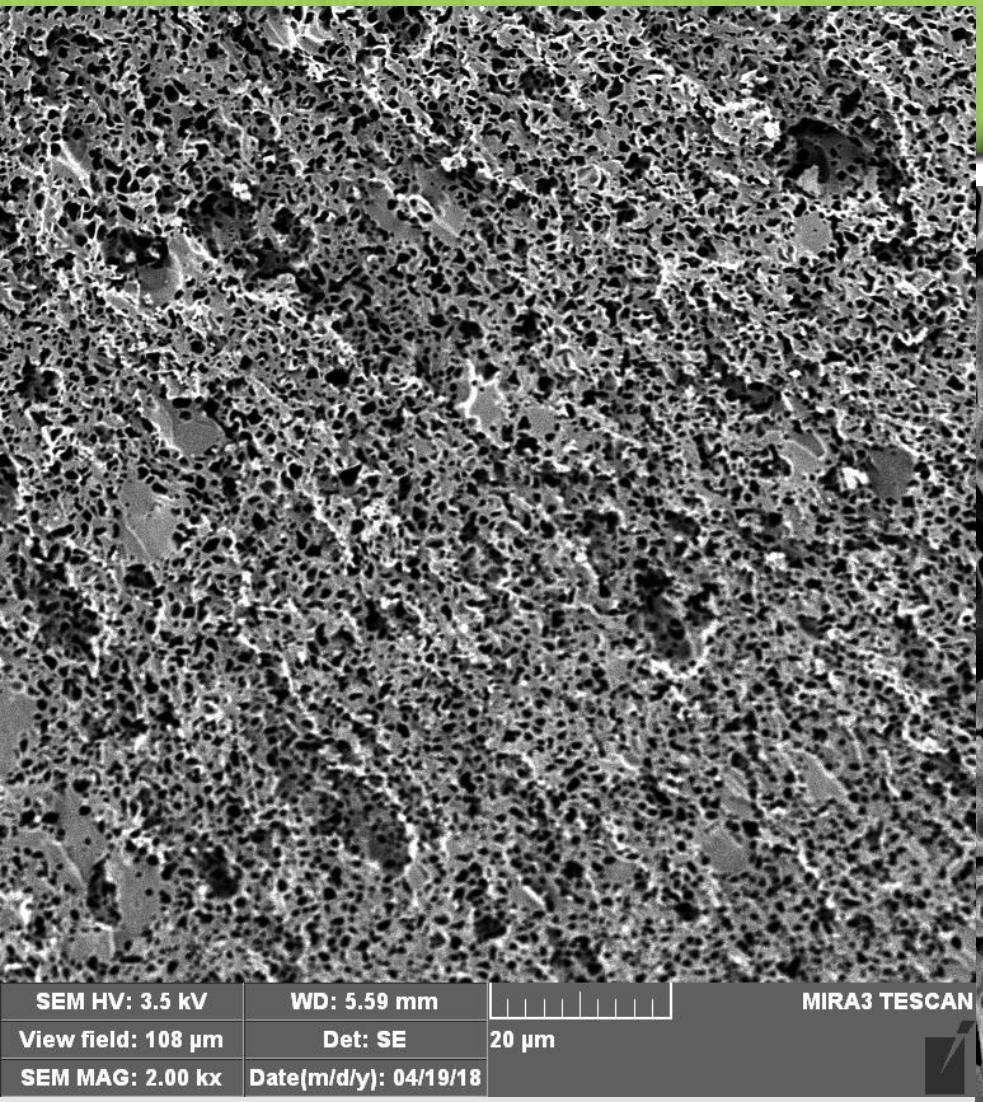
- The course of the modification of lignin was confirmed by **FTIR**, nuclear magnetic resonance (**NMR**) spectroscopy and X-ray photoelectron spectroscopy (**XPS**)
- The porous structures and morphology of obtained LMS were investigated by scanning electron microscopy (**SEM**), as well as via Brunauer-Emmett-Teller surface area analysis (**BET**) and Barrett-Joyner-Halenda (**BJH**) pore size and volume analysis
- X-ray diffraction analysis (**XRD**), thermo-gravimetric analysis (**TGA**)
- Amino-group content determined *via* ″back″ **(indirect) titration**
- Transmission electron microscopy (**TEM**) for analysis of MnO_2 and Fe_3O_4 nanoparticles
- **Adsorption** experiments (**batch** and **column** studies) were made with diclofenac (DCF), *Ni(II), Cd(II), arsenate and chromate ions*

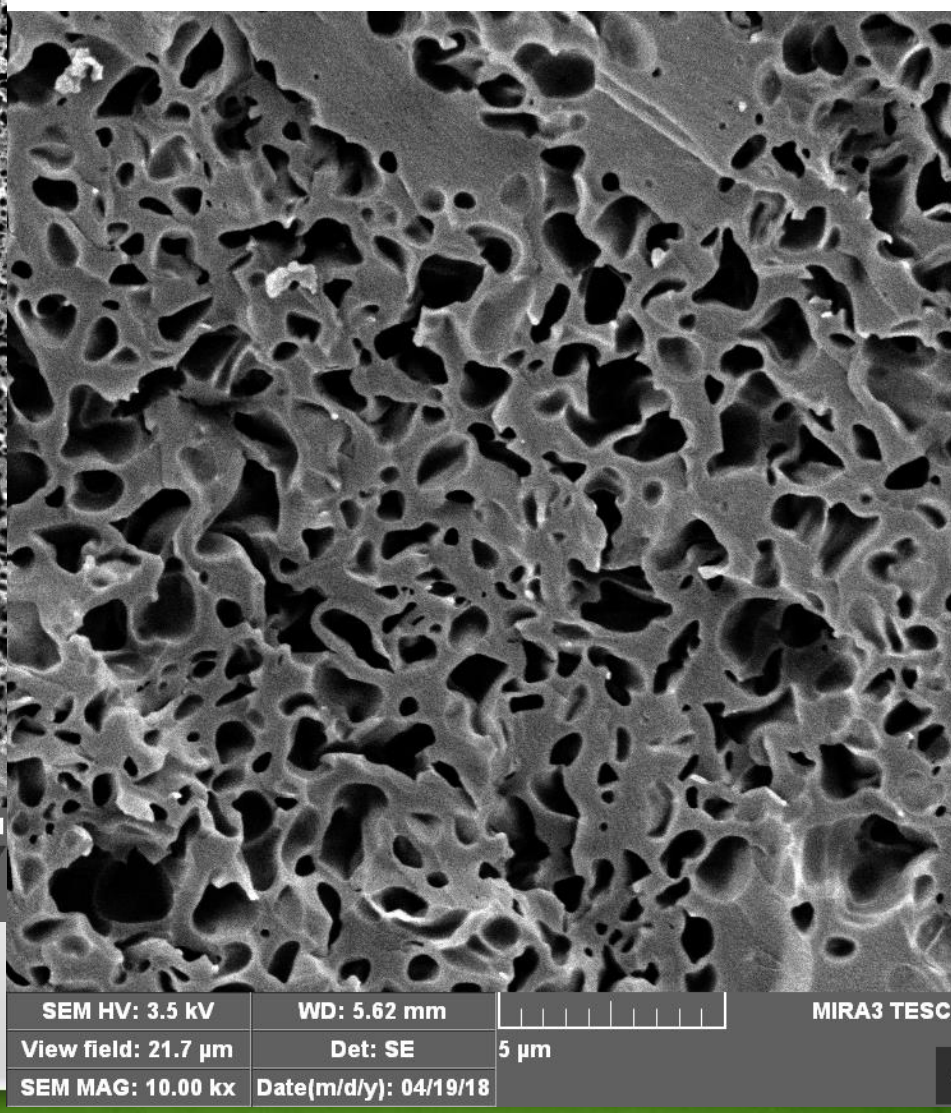
SEM view

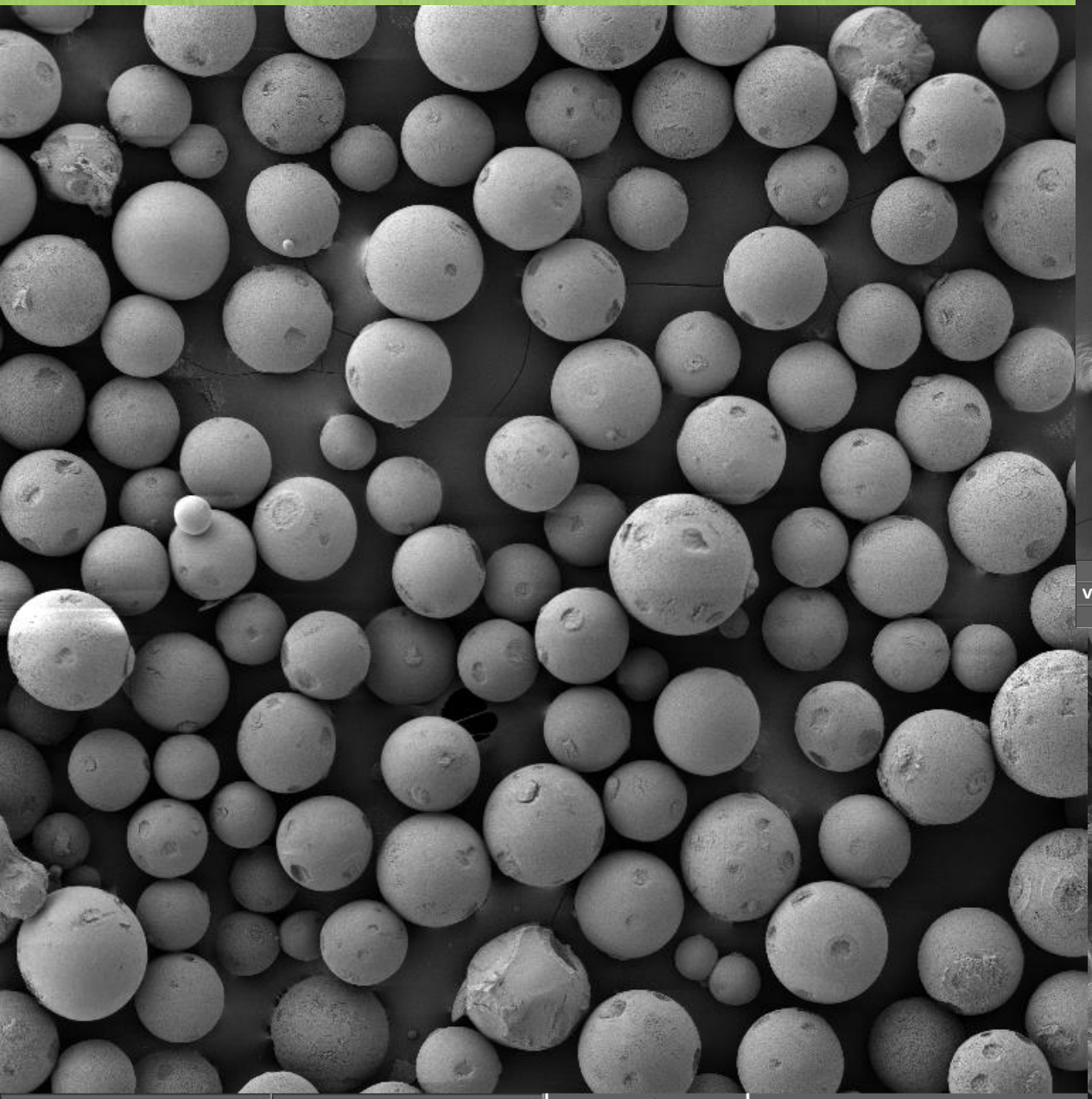


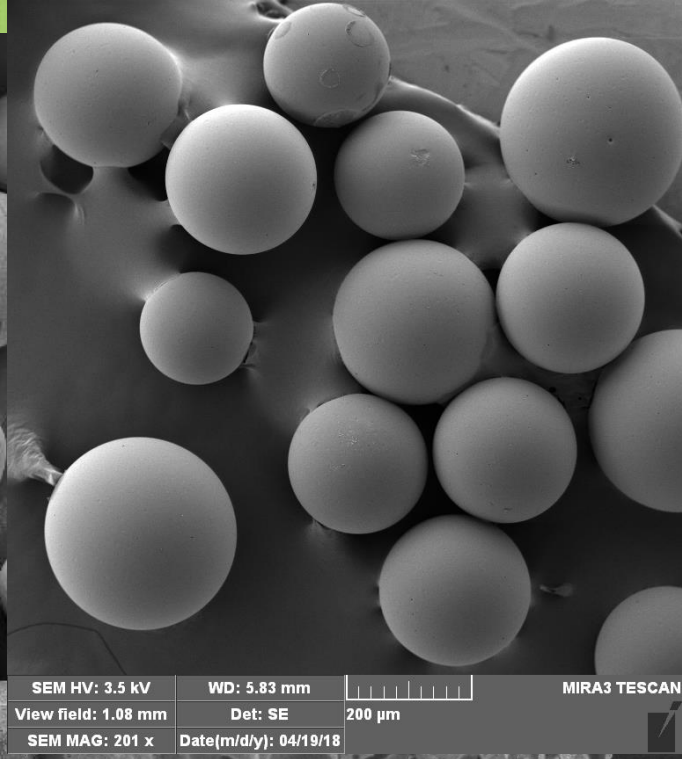


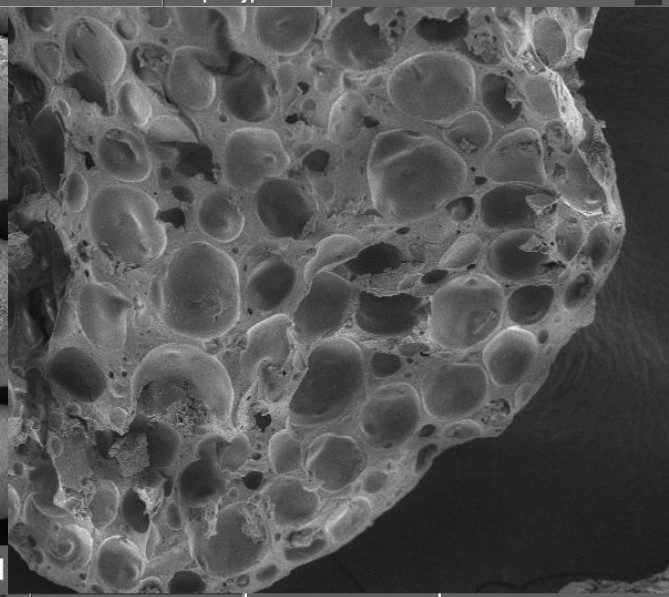
High porosity



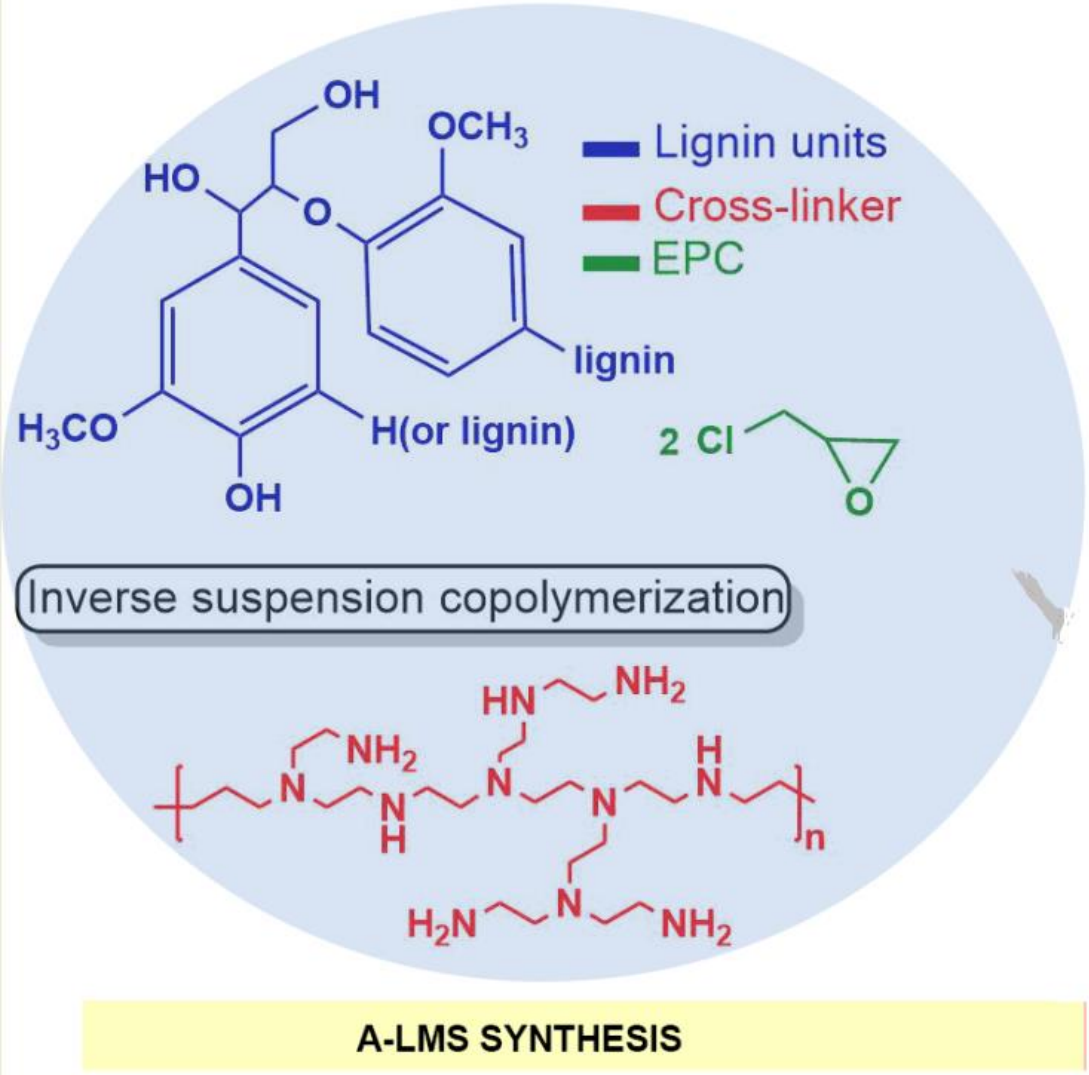



SEM HV: 3.5 kV
WD: 6.10 mm
MIRA3 TESCAN
View field: 1.08 mm
Det: SE
200 µm
SEM MAG: 200 x
Date(m/d/y): 04/19/18


SEM HV: 3.5 kV
WD: 5.83 mm
MIRA3 TESCAN
View field: 1.08 mm
Det: SE
200 µm
SEM MAG: 201 x
Date(m/d/y): 04/19/18


WD: 5.92 mm
MIRA3 TESCAN
Det: SE
100 µm
Date(m/d/y): 04/19/18

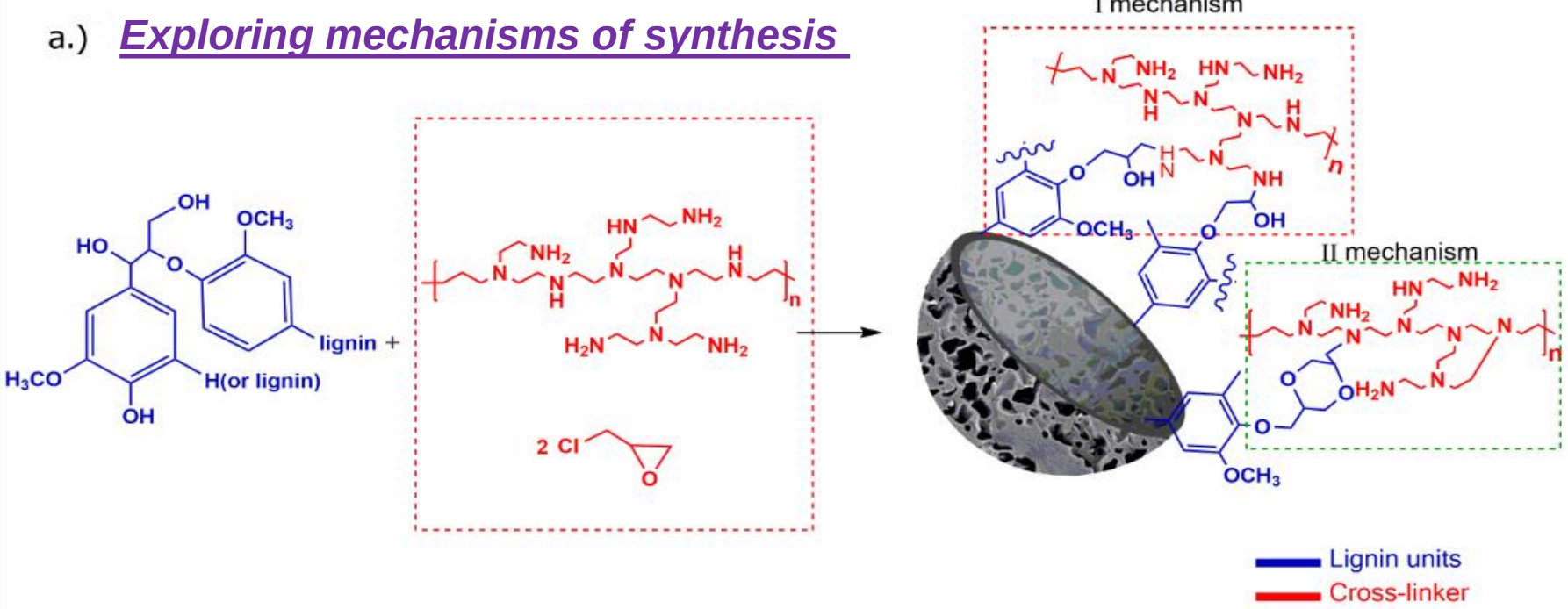
Inverse suspension copolymerization



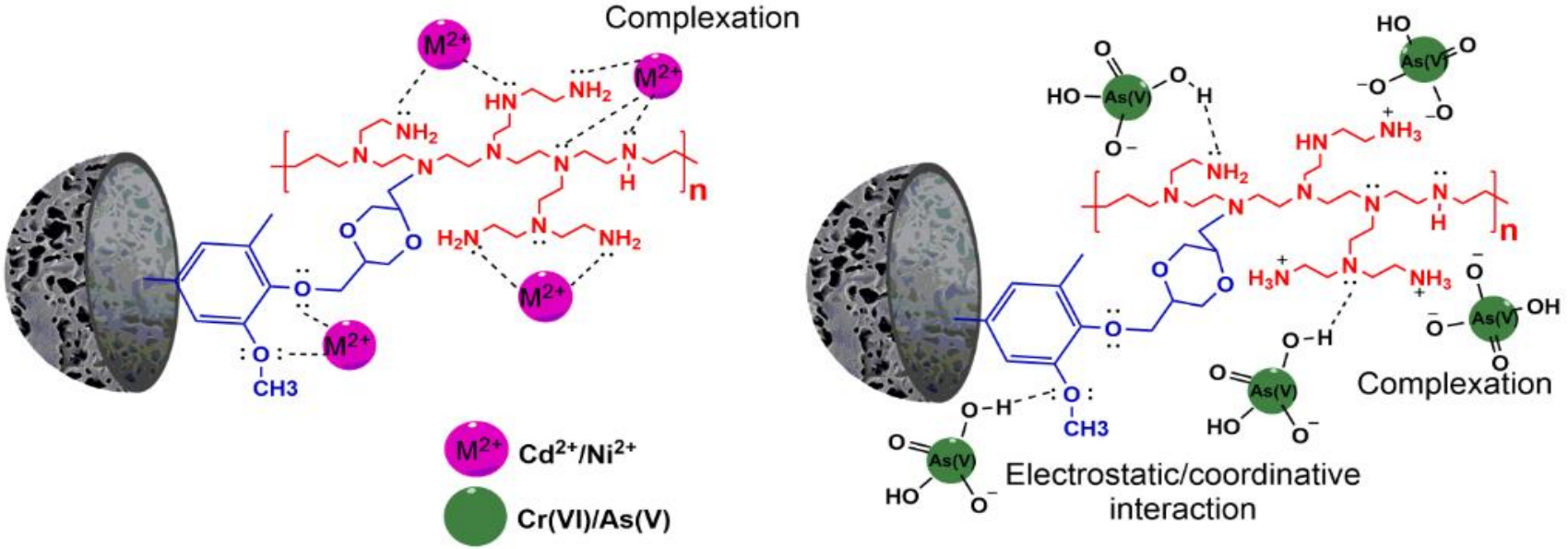
A-LMS SYNTHESIS

- kraft lignin
- poly(ethylene imine) grafting-agent
  - for amino-functionalization
- epoxy chloropropane cross-linker
- sodium alginate emulsifier (1, 5 and 10 wt.%)

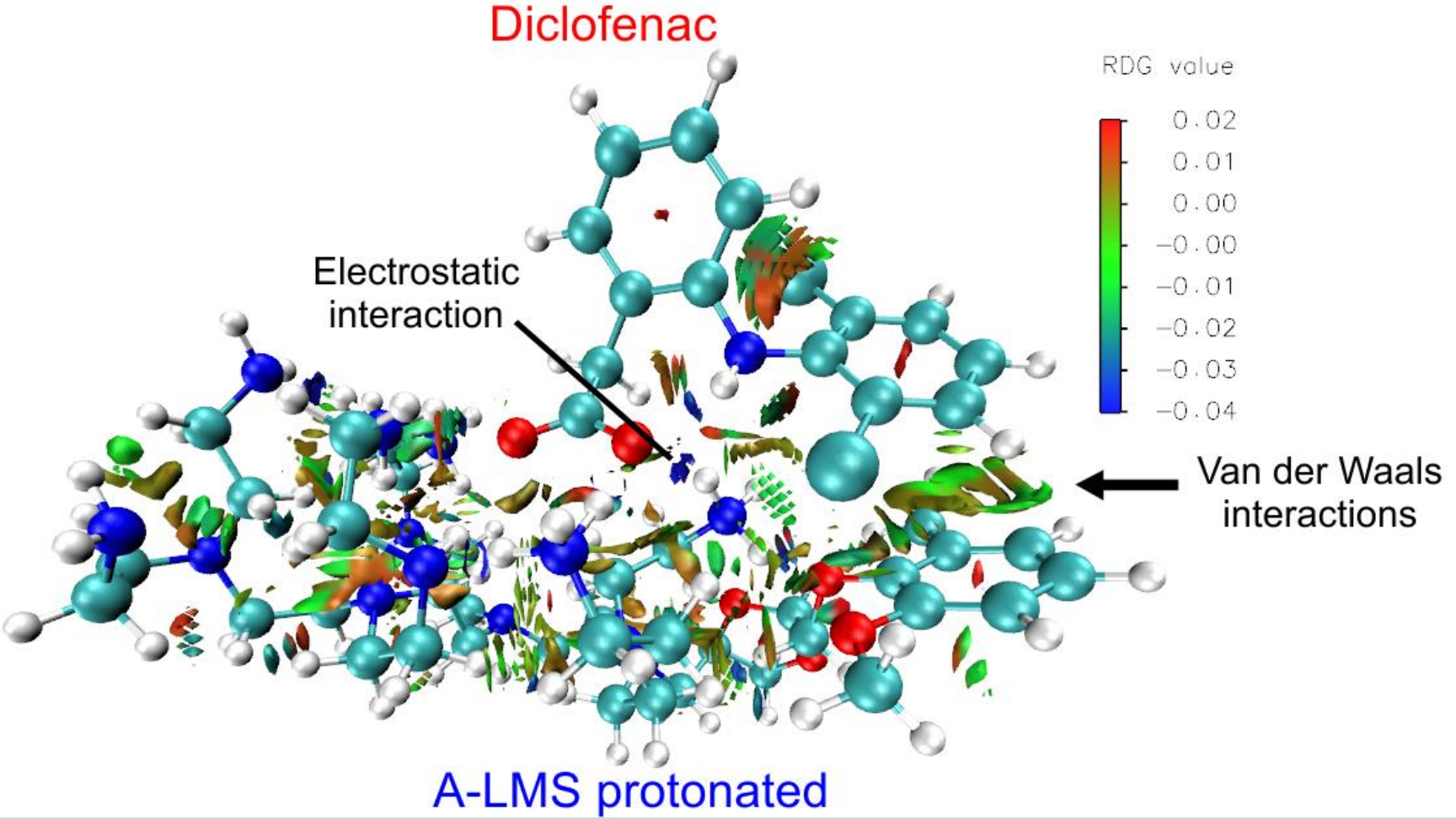
a.) **Exploring mechanisms of synthesis**



b.) **Exploring mechanisms of heavy-metal ion adsorption**



Exploring the diclofenac adsorption



Adsorption isotherms, kinetics and column study

- Langmuir, Freundlich and Dubinin-Radushkevich adsorption isotherm fitting data, obtained at 298, 308 and 318 K
- Thermodynamic parameters of adsorption analyzed
- Kinetic study was done with the following kinetic models:
  - PSO,
  - Roginsky-Zeldovich-Elovich (Elovich)
  - Dunwald-Wagner (DW)
  - Homogenous Solid Diffusion (HSDM), as well as
  - Intra-particular Weber-Morris (W-M) Model
- Fixed-bed column studies using Bohart-Adams, Yoon-Nelson, Thomas and Clark models
- Pore surface diffusion modeling (PSDM) – predicting the full-scale packed system

Conslusions

- The proposed LMS are **eco-friendly**, **cost-efficient** and **effective** adsorption materials
- Proven presence of **functional groups** and well-developed, highly **porous structure**
- LMS showed an **excellent adsorption capacity** towards *diclofenac* and heavy-metal ions: *Ni(II), Cd(II), arsenate and chromate ions*
- DCF (**151,13**) >> Cd^{2+} (74,84) > Cr(VI) (54,20) > As(V) (53,12) > Ni^{2+} (49,42 mg g^{-1})
- Formulation of lignin-based **new bio-polymer materials** increase the contribution of **renewable** materials, **from waste resources**, in wastewater treatment processes

Thank you!

ELSEVIER

International Journal of Biological Macromolecules

Volume 156, 1 August 2020, Pages 1160-1173

Novel amino-functionalized lignin microspheres: High performance biosorbent with enhanced capacity for heavy metal ion removal

Ana L. Popovic [a], Jelena D. Rusmirovic [b, c], Zlate Velickovic [d], Zeljko Radovanovic [c], Mirjana Ristic [a], Vera P. Pavlovic [e], Aleksandar D. Marinkovic [a]

Show more

https://doi.org/10.1016/j.ijbiomac.2019.11.152

Get rights and cont

ELSEVIER

Journal of Industrial and Engineering Chemistry

Available online 10 October 2020

In Press, Journal Pre-proof

Kinetics and column adsorption study of diclofenac and heavy-metal ions removal by amino-functionalized lignin microspheres

Ana L. Popovic [a], Jelena D. Rusmirovic [b], Zlate Velickovic [c], Tihomir Kovacevic [b], Aleksandar Jovanovic [a], Ilija Cvijetic [d], Aleksandar D. Marinkovic [a]

Show more

https://doi.org/10.1016/j.jiec.2020.10.006

Get rights and content

lignoCOST