

# A Novel Insight into the Domain Architecture of Transition-Metal Cross-Linked Alginates: Paramagnetic Solid-State NMR Spectroscopy

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## INTRODUCTION

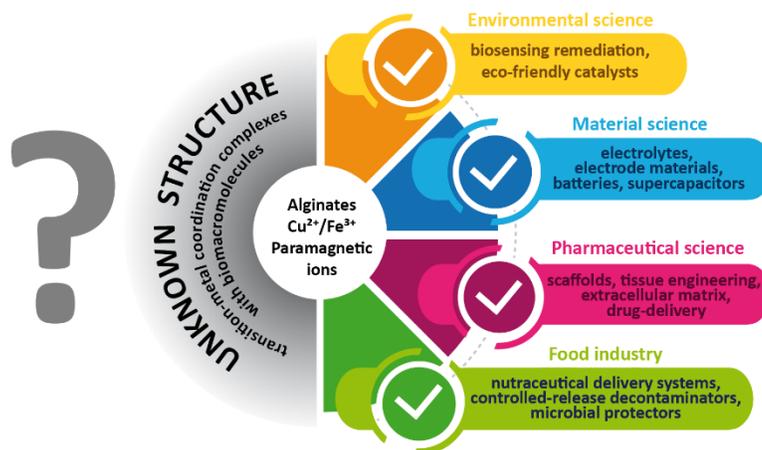
Due to the regenerative nature of metal-coordination bonds, transition-metal cross-linked alginates have become indispensable in addressing a range of technological challenges. However, as given by their amorphous character and the paramagnetic nature of many transition-metal ions, the crucial knowledge for optimizing their physicochemical properties – i.e. coordination geometry, and atomic-resolution structure – have long remained elusive to the conventional solid-state NMR and x-ray diffraction techniques.

## EXPERIMENTAL/THEORETICAL STUDY

To overcome this problem, we have utilized an advanced strategy based on ultra-fast magic angle spinning (UF/MAS) NMR allowing to remove extreme signal broadening caused by the interactions of nuclear spins with unpaired electrons. This way we have focused on obtaining up to now unreported data on molecular structure, network density and domain architecture of multicomponent alginate systems cross-linked by paramagnetic Cu<sup>2+</sup>/Fe<sup>3+</sup> ions.

## RESULTS AND DISCUSSION

Although the majority of alginate matrix was found to be regularly populated by Cu<sup>2+</sup> or Fe<sup>3+</sup> ions, we have also identified large areas of metal-ion-free alginic acid chains forming acidic gels. This finding thus revealed heterogenous character of the networks, which contain non-negligible content of nanosized domains of acidic alginate gels, which are phase-separated from the Cu<sup>2+</sup>/Fe<sup>3+</sup>-crosslinked alginate matrix. Surprisingly a high proportion of protonated carboxyl units COOH coexisting with the deprotonated carboxylate COO<sup>-</sup> groups was revealed. Additional structural data were then derived from <sup>1</sup>H and <sup>23</sup>Na UF/MAS NMR spectra in which unusual signals at very high-frequency regions (ca. 120-70 ppm) were detected. These down-field shifted NMR signals, which resulted from the hyperfine coupling of nuclear spins with unpaired electrons, indicated well-defined binding of Cu<sup>2+</sup>/Fe<sup>3+</sup> ions with uronic units. DFT calculations then suggested that Cu<sup>2+</sup>/Fe<sup>3+</sup> ions accompanied by water molecules coordinate with uronic units through carboxyl, carboxylate, and hydroxyl groups, adopting the octahedral geometry.



## CONCLUSION

It is thus clear that UF/MAS methodology allows obtaining sufficiently resolved ss-NMR data even for paramagnetic systems which are far below the detection limits of conventional ss-NMR techniques. The present research thus has ambitions to provide one the first experimentally confirmed representations of the complex interactions in alginate systems crosslinked by paramagnetic transition-metal ions. These findings then can have a direct implication for the synthesis of novel functional materials based on carbohydrate polymers.

## ACKNOWLEDGMENTS

This work was supported by the project **New Technologies for Translational Research in Pharmaceutical Sciences /NETPHARM**, project ID CZ.02.01.01/00/22\_008/0004607, co-funded by the European Union.