biopolymers from water



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Fabrication of PHA-based release systems for agrochemicals



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Motivation

Agricultural sustainability is critical as global food demands rise



alongside evolving global environmental challenges. Agrochemicals, such as fertilizers, herbicides and pesticides, are central to modern agriculture practices. However, their (over)use leads to runoff and leaching – risking groundwater contamination and ecosystem disruption. Innovative release systems are needed to ensure that benefits from applied agrochemicals are possible without any environmental risks.

Polyhydroxyalkanoates (PHAs) are a family of biobased polyesters produced naturally by many species of microorganisms. They occur as intracellular storage granules for carbon and energy. The inherent biodegradability and thermoplastic properties of PHAs make them ideal engineering materials for the fabrication of agrochemical delivery systems. Furthermore, emerging EU legislation on fertilizing products (Regulation (EU) 2019/1009) motivates their use in these developments. The regulation is intended to ensure strict compliance with biodegradability criteria, with an effort to prevent microplastic pollution [1].

> During recovery with "PHA-poor" solvents, a viscous polymer solution is formed. Upon cooling, the solution undergoes gelation where PHA forms a stable semi-crystalline 3D polymer network with trapped solvent (Fig.1). Gelation is (thermo)reversible and presents the basis of an opportunity to develop innovative methods for making biodegradable PHA-based controlled-release agrochemical systems. Fabrication methods will depend on the interplay between PHA properties (molecular weight, crystallinity, co-polymer composition, polydispersity) and "PHA-poor" solvent characteristics, which influence gelation behaviour. There is value in the dual use of the extraction solvent by integrating PHA recovery and fabrication of applications.

Technological challenges

PHA can be produced through fermentation, using (wastederived) carbon-rich substrates. Engineered bioprocesses enable large-scale production, yielding batches of PHA-rich biomass. A step of recovery and purification is required to prepare the PHA for use in applications. PHA recovery has traditionally employed halogenated "PHA-good" solvents that are effective in solubilizing PHA from the biomass. However, the use of halogenated solvents poses environmental and health risks. Alternatively, nonhalogenated solvents are considered "greener" and offer a more sustainable approach to the recovery process, requiring elevated temperatures to effectively dissolve the PHAs, thus being referred to as "PHA-poor" solvents [2].



Research goals

This project aims to advance a fundamental understanding of PHA gelation. That understanding will be applied to integrate PHA extraction with innovative fabrication methods using "PHA-poor" solvents to fabricate PHA-based agrochemical release systems. This research will advance on ongoing efforts to scale up PHA production using regional municipal wastewater and organic waste residuals as renewable resources [3]. Thus, the project impact is directed to resource management and supporting regional circular economies with products and services for sustainable agriculture and water quality protection (Fig. 2).

Fig. 1 Integration of "greener" solvent PHA recovery process steps with solution processing for preparation of PHA-based delivery systems.

[1] Regulation (EU) 2019/1009, https://eur-lex.europa.eu/eli/reg/2019/1009/oj/eng.
[2] Vermeer et al. (2022). *J. Environ. Chem. Eng.*, 10(6), 108573.
[3] Estévez-Alonso et al. (2021). *Bioresour. Technol.*, 327, 124790.

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