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Engineering biodegradable coatings for sustainable fertilisers

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ABSTRACT

With the pressures of a changing global climate and ever-growing population, the need for sustainable agricultural practices that increase crop yields while decreasing greenhouse gas emissions are critical. Currently used practices to increase yields can often be problematic due to low nitrogen use efficiency or a potential overreliance on agrichemicals that can alter the community composition of a given ecosystem, although this is typically system and situation dependent. As such, the next generation of enhanced efficiency fertilisers that combine chemical, materials engineering and biological components are likely to be a game changer. Integral to their success is a better understanding of how plant–soil microbiomes interact with the new enhanced efficiency fertilisers, and how we can best tailor the fertilisers to suit different plant–soil combinations. In particular, the biodegradation properties of new fertiliser coatings must be given careful consideration so as to not further burden agricultural soils with microplastics or cause ecotoxicity problems. This perspective proposes novel, interdisciplinary strategies to generate highly efficient, biodegradable fertiliser coatings for use in the agricultural sector.

Keywords: agriculture, biodegradation, biotechnology, fertilisers, plant–microbiome interactions, polymers, soil microbiology, sustainability.

The challenges of feeding the world on finite agricultural land

With global populations set to reach 10 billion by 2050,[1] there is increasing pressure to match food production within existing agricultural lands in the face of a changing global climate. Integral to global food security is an increasing reliance on synthetic fertilisers to improve crop yields,[2] while simultaneously reducing their negative environmental impacts.[3] Though there have been recent shifts towards designing fertilisers with enhanced efficiency[1,4,5] including those that have been coated with a polymeric substance such as metal–phenolic networks,[6,7] these have not been widely adopted by the global agricultural industry. In addition, strategies to further increase crop yields, such as the deployment of pesticides, herbicides and enzymatic inhibitors,[8,9] may also lead to disruptions in the balanced plant holobiont (i.e. the collection of microorganisms such as bacteria, fungi, archaea and protists, that form close associations with the plant host).[10,11] Thus, the design of new generation fertilisers must take into consideration sustained and tailorable release profiles, the degradation of coatings and ecotoxicity potential, as well as the potential benefits of incorporating probiotic microorganisms into engineered coatings to enhance plant performance.

Among the major design challenges for the development of new fertilisers is the composition of coatings that cannot only slow the release of the internal nitrogenous compound, but also can be completely biodegraded by indigenous soil microorganisms. This remains an understudied challenge within both the fertiliser and agricultural industry, as the microorganisms that comprise plant holobionts are often host or soil specific,[12] and may not be shared among different crop types.[13,14] As such, innovative microbial solutions are required to ensure that newly developed biopolymeric fertiliser coatings can be degraded by a wide range of microorganisms native to different soil types and plant species. In addition, ensuring that the polymers are completely degraded and do not generate microplastics[15–17] is paramount to ensure that ecosystems are not further burdened. We thus outline a cross-disciplinary strategy combining materials engineering and plant–soil microbiology approaches to generate innovative hybrid chemical–biological fertilisers for use in Australian agricultural systems.

Current state of agricultural practices and potential innovation strategies

Current practices within the agricultural industry are heavily weighted towards the usage of conventional fertilisers that are typically applied in liquid form or as uncoated granules.[4]

As Australia possesses one of the highest nitrogen footprints in the world (~47 kg of nitrogen per capita per year), with food production comprising the largest component,[18] it is of great importance to develop new products to reduce the environmental and socioeconomic impacts of fertiliser use.[1] It is well established that intensive and improper use of nitrogen-based fertilisers can lead to numerous undesirable effects including mining of soil nitrogen in low-rainfall cropping areas,[18] nitrate leaching into waterways causing eutrophication,[19] and nitrous oxide and ammonia emissions into the atmosphere, contributing to global warming.[20] With the current cost of developing, producing and deploying enhanced efficiency fertilisers up to 10 times higher than that of commercial fertilisers within the agricultural sector,[5,21] the use of these commercial fertilisers will continue to be widespread and are unlikely to decrease unless next-generation fertilisers are comparably priced and are higher efficiency.

Within the agricultural sector, three major approaches are currently used to mitigate excess nitrogen loss within cropping lands as well as increase crop nitrogen use efficiencies: (1) addition of chemical urease and nitrification inhibitors[4,10,11]; (2) utilisation of the 4R Nutrient Stewardship concept (right source of nutrients, at the right rate, at the right time and in the right place)[22]; and (3) use of physical barriers to slow the release of fertilisers.[7,23] Although the benefits of urease and nitrification inhibitors have been well documented,[5,11] the use of polymer-coated fertilisers has been comparatively less studied. The effectiveness of polymer-coated fertilisers specifically was demonstrated to have negative to negligible positive effects on drylands and grasslands, and was highly influenced by soil pH.[5] This is a concerning phenomenon for translation into the Australian agricultural sector, which is predominantly grasslands and drylands.[24,25] Additionally, the type of polymer used in the coating needs to be carefully selected to ensure that it is capable of natural degradation, meets national biodegradability standards and by-products do not have ecotoxicological effects. It is important to note that currently there are no global standards governing the biodegradation parameters of fertiliser coatings. More work is required to understand the effects of additives on polymer degradation by microorganisms, as numerous reports have highlighted deleterious effects of microplastics on soil organisms and functions.[26] Subsequently, the question remains, can enhanced-efficiency polymer-coated fertilisers be generated for use within the Australian agricultural industry, taking into consideration the unique properties of Australian soils?

Upcoming multidisciplinary approaches to engineering biodegradable fertiliser coatings

The effectiveness of controlled release fertilisers could potentially be improved by the incorporation of biological additives, such as plant-growth promoting bacteria (PGPB) as well as polymer-degrading microorganisms (PDMs). Biofertilisers, or microbial inoculants, can be split into two major classes, rhizobia-based inoculants that are primarily applied to legumes, and non-rhizobia based inoculants to non-legumous crops. Non-rhizobia biofertilisers in the form of peat or liquid supplements have been demonstrated to increase the yield of numerous crops including soybeans, maize and rice, though positive effects can vary greatly across different applications.[27,28] Although biofertilisers have been implemented for decades,[28] they are scarcely used within the Australian agricultural sector aside from in forage legumes.[27] In particular, the uptake of these biofertilisers has been sporadic in wheat-producing nations and has had inconsistent results between countries, indicating that species-specific interactions between plant subtypes and microbial inoculants might be critical to consider.[27]

Similarly, the discovery and characterisation of PDMs is rapidly growing in response to the overuse of plastics worldwide, though their efficiencies in different ecosystems remains understudied.[16] A recent review by Gambarini *et al.* determined that, although the degradation capacity for microorganisms is taxonomically widespread, experimental evidence of this has been minimal so far.[29] Some of the better-characterised PDMs include *Ideonella sakaiensis*, which has been shown to degrade polyethylene terephthalate, numerous species within the order Bacillales, which are capable of polypropylene and polystyrene degradation, and species from the *Amycolatopsis* genus, which have been shown to degrade polylactic acid polymers.[29] In particular, the conditions within which polymers are partially or completely degraded can differ extensively between different polymer types, with synthetic polymers derived from fossil fuels (e.g. polyethylene terephthalate, polypropylene and polystyrene) typically only degraded by microorganisms under specific conditions.[15,29] Conversely, coatings developed from biopolymers, polymers that are made from renewable resources (e.g. polyhydroxybutyrate) would likely be better candidates as they have a greater biodegradation potential than synthetic polymers.[29] Thus, careful consideration of polymer type as well as the *in situ* degradation capacity of the agricultural soil tested must be at the forefront of the generation of fertiliser coatings. Soil properties, such as pH and organic carbon content, in conjunction with the plant species grown must also be considered as these can drastically alter the composition of microorganisms within the rhizosphere.[12] As such, the testing of multiple soil types and incubation conditions on the same polymer type must be carried out to assess the generalisability of degradation across different agricultural systems. It is likely that multiple polymer and microbial combinations need to be generated for each plant–soil combination due to specific nature of plant–soil–microbiome interactions.[13] Thus, an ongoing challenge is finding microbial combinations that will promote the growth of crops, remain in the soil long term and are able to be incorporated into existing fertiliser delivery strategies such as coatings.

Our strategy for developing next-generation smart fertilisers is to use a multidisciplinary approach, combining complimentary microbiological, chemical and materials engineering strategies. As demonstrated by the schematic in Fig. 1, we aim to combine culture-independent and culture-dependent microbiological techniques with materials engineering to develop economically viable smart fertilisers capable of increasing yields and reducing nitrogen losses. Determination of soil physicochemical properties as well as overall microbial community structure could potentially

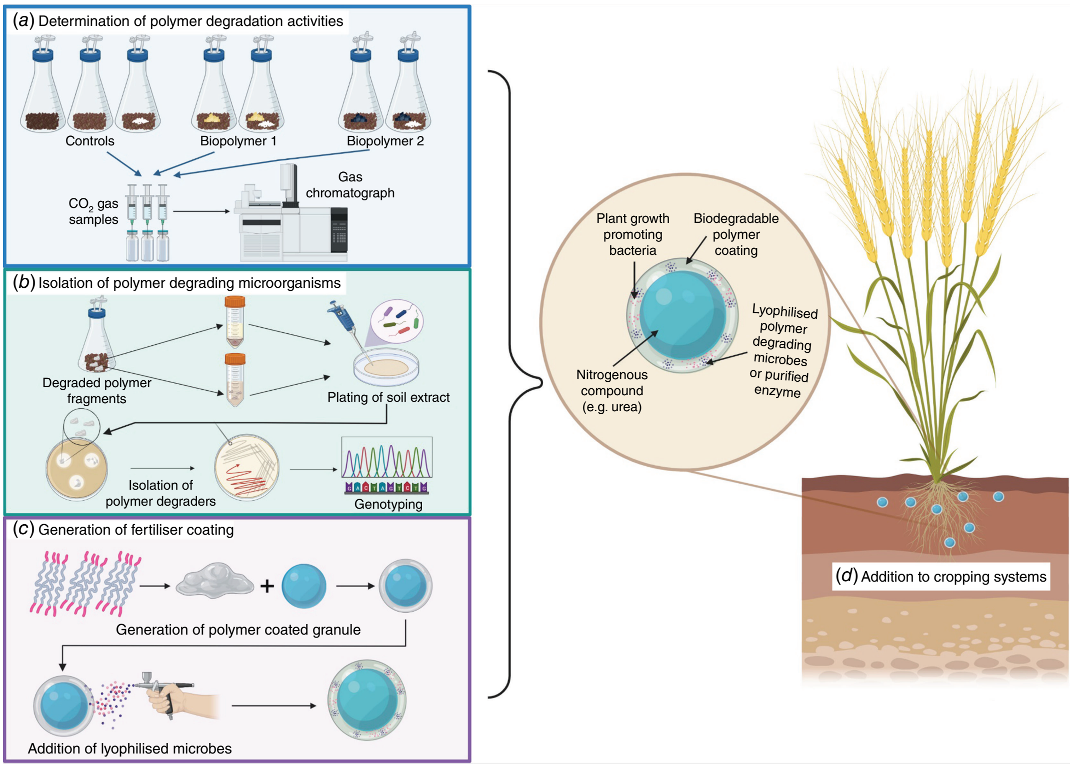

Fig. 1. Schematic highlighting the multidisciplinary strategy to generate, test and implement new biodegradable fertiliser coatings. Our approach to designing new fertiliser coatings includes the following: (*a*) *in situ* determination polymer degrading capacity of chosen polymer and potential polymer-degrading microorganisms using a combination of gas chromatography and visual observation techniques, (*b*) isolation of polymer degrading microorganisms using traditional culturing methods and genome-informed culturing methods, (*c*) materials engineering approaches to generate new biodegradable polymers and coating of granulised fertiliser, followed by external application of lyophilised polymer degrading and plant-growth promotion microorganisms or crystallised polymer degradation enzymes, and (*d*) deployment of smart fertiliser into cropping systems such as wheat fields. These smart fertilisers will be customised for each major soil type as well as plant species to maximise efficiency. Figure created using BioRender.

enable genome-informed cultivation strategies to target both PGPB and PDMs specific to each major Australian crop species–soil combination (Fig. 1*b*).[30] *In situ* biodegradation studies, assayed by gas chromatography (GC) of CO_2 production and scanning electron microscopy (SEM), using biodegradable polymer candidates will also inform downstream coating design, with candidates able to be degraded by multiple soil types and in multiple conditions prioritised (Fig. 1*a*). The direct measurement of degradation by GC and SEM will be accompanied by additional, complementary analytical techniques, such as complete soil physiochemical analysis and Fourier-transform infrared spectroscopy. Partially degraded polymers will then be used as the starting inoculum for PDM isolation using minimal media with fresh polymer as the sole carbon source (Fig. 1*b*). Isolates will then be phenotyped to determine the mechanism by which polymer degradation was occurring, with the potential to purify degradation enzymes. Within a coating, it is theoretically possible to include urease and nitrification inhibitors[1] as well as a microbial cocktail of lyophilised PGPB and PDM or purified enzyme (Fig. 1*c*). This would allow for controlled release of the encapsulated chemical fertiliser (e.g. urea) because of the degradation effects of the PDM, the inhibition of major enzymatic pathways leading to nitrogen losses and the delivery of PGPB directly to the rhizosphere (Fig. 1*d*).

Concluding remarks

With an increasing global population and a changing global climate, addressing food scarcity through innovative microorganism-forward agriculture is paramount. Only through a deep understanding of plant–soil–microbiome interactions and using multi-disciplinary approaches can new biodegradable polymer coatings for chemical fertilisers be generated. This new generation of enhanced efficiency fertilisers should be tailored to specific plant–soil combinations to obtain the best yields and nitrogen use efficiencies while also being a viable economic alternative to currently used chemical fertilisers.

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