

## CRITICAL REVIEW

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## Exploration of biodegradable polymeric particles in agriculture: a holistic approach for sustainable farming

Kunal Verma, Chandrani Sarkar and Sampa Saha  \*

Conventional agricultural methodologies often rely on excessive application of fertilizers, pesticides, and water, resulting in adverse environmental consequences such as air/water/soil pollution, soil degradation, etc., thereby diminishing farming efficiency and profitability. The growing demand for sustainable agricultural practices has intensified researchers' interest in exploring biodegradable polymeric particles (BPPs) due to their ability to improve agrochemical delivery, enhance soil health, and mitigate environmental impacts. This review critically examines the state of the art in the design, fabrication, and application of BPPs for agriculture to accomplish sustainable farming. It highlights their significance in enabling controlled release systems, soil improvement, and plant stress tolerance. Key fabrication techniques such as emulsion solvent evaporation, anti-solvent nanoprecipitation, ionotropic gelation, and spray drying are compared based on their scalability, cost-efficiency, and suitability for producing particles with tailored properties. The influence of particle size, shape, and morphology on application efficiency and their biological interactions are thoroughly analyzed, emphasizing the importance of design in optimizing performance. This review also explores the challenges associated with adopting BPPs, including scalability, cost, regulatory compliance, etc., and proposes future directions for advancing their development. By addressing critical gaps and presenting innovative strategies, this review provides a comprehensive framework for integrating biodegradable polymeric particles into sustainable agricultural practices.

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### Environmental significance

The adoption of biodegradable polymeric particles (BPPs) in agriculture presents a significant advancement toward sustainable farming practices. By enabling controlled release of agrochemicals such as fertilizers and pesticides, BPPs reduce environmental pollution, enhance soil health, and minimize chemical runoff into water bodies. These particles decompose naturally, thus eliminating the long-term environmental hazards posed by conventional plastics and synthetic materials. The use of BPPs aligns with the global push for reducing reliance on non-renewable resources and limiting the ecological impact of traditional agricultural methods. This holistic approach supports the goal of maintaining biodiversity and soil fertility while ensuring efficient resource use in farming systems.

## 1. Introduction

The increasing demand for sustainable agricultural practices has driven significant interest in the development of innovative biodegradable polymeric particles for the agricultural sector.<sup>1,2</sup> In recent years, the use of biodegradable polymeric particles in agriculture has been expanded, encompassing various applications such as controlled-release formulations, soil improvement, and crop protection.<sup>3-7</sup> For instance, these particles are designed to deliver agrochemicals, such as pesticides and fertilizers, in a controlled manner, thus enhancing their efficacy and mitigating their adverse effects on the environment.<sup>8</sup> The

controlled release of agrochemicals not only improves crop yield and quality but also reduces the frequency of applications, thereby lowering the overall chemical load on agricultural fields and their toxic side effects.<sup>9</sup>

Traditional farming methods, characterized by intensive chemical inputs and indiscriminate resource consumption, have proven unsustainable, polluting waterways and contributing to climate change.<sup>10-12</sup> Moreover, the use of conventional non-degradable plastics or polymers in the agricultural sector has been associated with a multitude of issues. The intensive use of plastics can impair soil fertility and lead to dwindling crop yields.<sup>13</sup> There is also the undesirable prospect of toxic additives leaching from plastics seeping into our food chain. In China, agricultural films are found to release 91.5 tons of PAEs (phthalic acid esters) from mulching and greenhouse films,

Department of Materials Science and Engineering, Indian Institute of Technology, Delhi, New Delhi-110016, India. E-mail: [ssaha@mse.iitd.ac.in](mailto:ssaha@mse.iitd.ac.in)

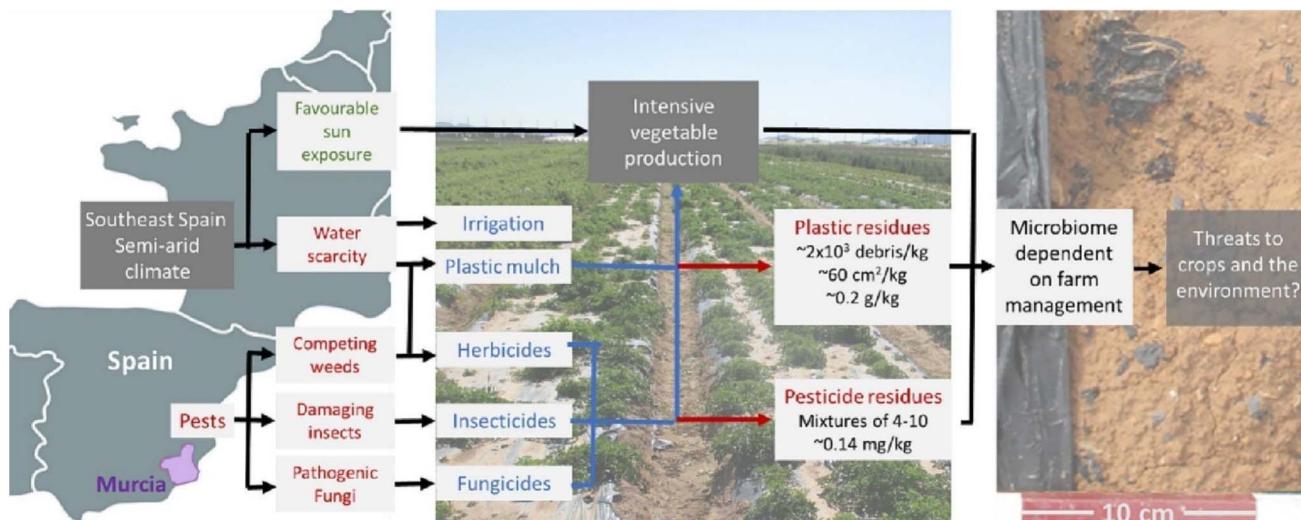


Fig. 1 Low-density polyethylene plastic mulch following kohlrabi harvest. The sides of the mulch film are buried in the ground, full removal is not feasible and over time debris builds up. Reused with permission from the author (CC BY).<sup>19</sup>

contributing to soil and vegetable contamination, respectively.<sup>14</sup> One of the most significant problems is the accumulation of these materials in soils, which can have diverse and long-term effects on crop production and quality.<sup>15</sup> Conventional mulch films (mainly polyethylene) accumulate leftover fragments from agricultural soils, which may negatively impact soil productivity and ecology (Fig. 1). Moreover, there is evidence that “non-degradable” mulches pose threats to human health and are found to be carcinogenic, mutagenic, endocrine disrupting and bioaccumulative.<sup>16</sup> Many experts have shown concerns about managing conventional plastics and replaced them with biodegradable polymers that decompose in soil through microbial activity, thus minimizing the accumulation.<sup>17,18</sup>

The integration of biodegradable polymeric particles into agricultural practices aligns with the principles of sustainable agriculture, which emphasize the efficient use of resources, reduction of waste, and protection of the environment. By leveraging these materials, farmers can achieve higher productivity while maintaining soil health and biodiversity. Moreover, the biodegradability of these polymers ensures that they do not accumulate in the environment, thus mitigating the long-term ecological impact associated with conventional plastics.<sup>20</sup>

Biodegradable polymers emerge as a promising sustainable platform in this endeavor, offering a multifaceted approach to addressing agricultural challenges.<sup>12,21-24</sup> These materials offer a promising alternative to conventional synthetic polymers, which are often associated with environmental pollution and long-term ecological damage. Biodegradable polymers, mainly derived from renewable resources, decompose naturally into non-toxic byproducts.<sup>25</sup> Biopolymers like cellulose and chitosan show promising results, when used for agricultural applications.<sup>26</sup> They are often procured from renewable resources or agricultural byproducts and offer economical and eco-friendly solutions.<sup>23,27-30</sup> Recent studies have also confirmed the soil biodegradability of poly(butylene adipate-co-terephthalate)

(PBAT), a synthetic polyester used in agriculture.<sup>31-34</sup> However, recent advancements in biodegradable polymeric materials in agriculture predominantly center on mulching applications.<sup>3,33,35,36</sup> Some studies explore their potential as superabsorbent polymers for soil remediation and agrochemical delivery.<sup>22,30,37,38</sup>

The adoption of biodegradable polymeric particles represents a significant step forward in addressing pressing agricultural challenges,<sup>39</sup> including nutrient inefficiency, environmental pollution,<sup>31,40</sup> and climate-induced stresses on crops. While numerous reviews focus on specific polymers<sup>2,3,41-43</sup> such as chitosan,<sup>44-47</sup> starch,<sup>30,46,48-50</sup> cellulose,<sup>51,52</sup> polylactic acid (PLA),<sup>53</sup> and their agricultural uses, others delve into individual applications like controlled-release fertilizers (CRFs),<sup>6,54,55</sup> hydrogels,<sup>56</sup> controlled-release pesticides,<sup>57-60</sup> and mulches.<sup>9,33,61</sup> However, there is a lack of comprehensive reviews that integrate all these aspects into a holistic framework. This review bridges that gap by providing an extensive analysis of the fabrication methods, polymers employed, and applications of biodegradable polymeric particles in agriculture.

This review systematically examines the diverse polymers used—ranging from naturally derived materials like cellulose and alginate to synthetic options like PLA and PCL—and their tailored applications. Each application, including nutrient delivery, pesticide encapsulation, soil enhancement, and plant growth regulation, is discussed with an emphasis on the active ingredients and the polymers used to formulate them. Additionally, the review incorporates environmental and economic considerations, highlighting how these materials can enhance agricultural sustainability while minimizing ecological impact. By discussing various fabrication techniques, application-oriented studies, and broader implications, this review offers a unified perspective on the potential of biodegradable polymeric particles to transform agricultural practices.



It provides a critical analysis of the state of the art, recent advancements, and challenges in utilizing biodegradable polymeric particles for agricultural purposes. Unlike previous reviews, which broadly cover polymer development, this work emphasizes the practical implementation of BPPs in agriculture, assessing their effectiveness, scalability, and environmental benefits. By identifying research gaps and providing actionable recommendations, this review aims to guide future innovations and promote the adoption of biodegradable polymeric particle based technologies for sustainable farming practices.

## 2. Significance of biodegradable polymeric particles in the agricultural sector

Biodegradable polymeric particles offer innovative solutions to overcome the limitations of conventional agricultural practices by enhancing efficiency, sustainability, and environmental stewardship.<sup>62</sup> Traditional fertilizer applications often lead to nutrient runoff by leaching and uneven distribution, causing environmental pollution and inefficient nutrient use. Encapsulating fertilizers in biodegradable polymeric particles allows for controlled release, reducing leaching and runoff while ensuring prolonged nutrient availability and improved plant uptake.<sup>63</sup>

Polymeric particles are always found to be better in terms of accuracy and effectiveness of agrochemicals' delivery than other forms of polymers.<sup>64</sup> Similarly, conventional pesticide applications face challenges such as drift, non-target effects, and the need for frequent reapplication due to rapid degradation or

wash-off. Biodegradable polymeric particles with encapsulated pesticides reduce drift, provide target applications more accurately, and produce slow-release formulations that extend efficacy without compromising the environment by lowering overall pesticide use.<sup>65-67</sup> Moreover, the release profile and responsiveness of particles can be tailored to meet the specific requirements of different plants.<sup>66,68,69</sup>

In large-scale irrigation systems, water and nutrient wastage is a common issue, particularly in water-scarce regions. Biodegradable polymeric particles enhance soil moisture retention<sup>70</sup> and deliver nutrients directly to the root zone, reducing water usage and nutrient wastage. While organic farming primarily relies on natural amendments like compost and manure, it could potentially benefit from biodegradable particles made from natural or biobased polymers, provided these particles contain only organic-compliant actives (without synthetic agrochemicals), such as seaweed extract,<sup>71</sup> spinosad<sup>72</sup> and other organic agrochemicals.<sup>73,74</sup> Since the majority of biodegradable polymers (resource synthetically or naturally) are biocompatible and FDA approved,<sup>75</sup> they can be thought to bring about benefits in sustainable farming without harming the soil health in the long run.<sup>42</sup> These particles provide controlled water and nutrient release, enhancing the efficiency of organic fertilizers while supporting the soil health and microbial activity.<sup>76</sup>

Mechanical weed control methods can be labor-intensive and less effective against certain weed types. However, biodegradable polymeric particles can deliver herbicides in a controlled manner, reducing the need for mechanical intervention without compromising the soil structure.<sup>60,77</sup> It is observed that polymeric particles have wide scope in agricultural fields ranging from agrochemical delivery to moisture retention capability of soils.

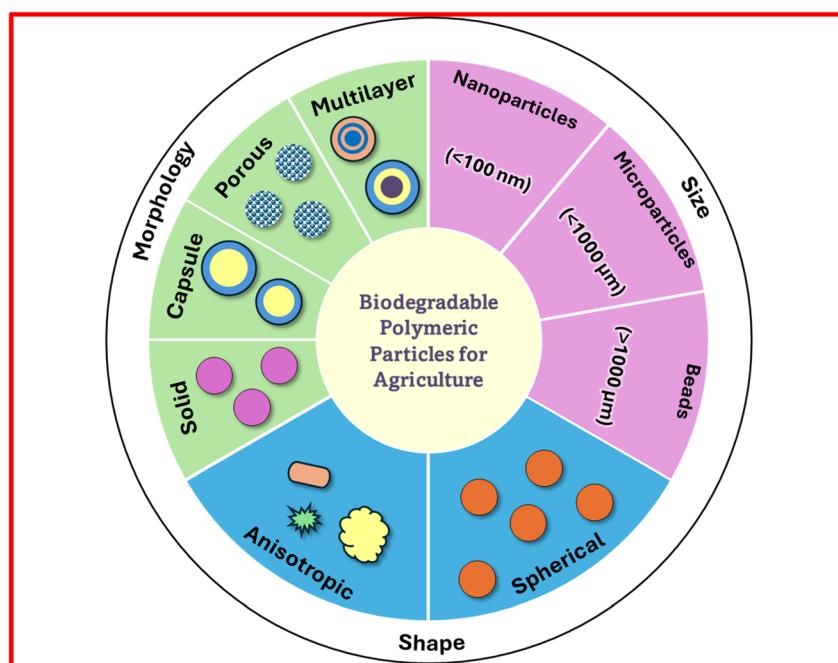


Fig. 2 Classification of biodegradable polymeric particles for agriculture.



### 3. Classification of polymeric particles

The size, shape, and morphology of polymeric particles are critical factors that influence their behavior in agricultural practices, including how they interact with plants and soils, their degradation rate, and the release profile of the active ingredients they contain. In this review, we have classified the biodegradable polymeric particles based on their size, shape and morphology (Fig. 2).

#### 3.1 Size

The size of the polymeric particles significantly impacts their function. For efficient uptake by plants or interaction with soil microbes, particles typically range from nanometers to micrometers in size and their action changes with their sizes. For instance, Lou *et al.* developed phoxim-loaded polyurethane microcapsules (MCs) with three different average diameters: 1.39  $\mu\text{m}$  (MC-S), 5.78  $\mu\text{m}$  (MC-M), and 23.60  $\mu\text{m}$  (MC-L). In the greenhouse experiments, MC-S and MC-M showed insecticidal activity primarily within the first three days, while MC-L maintained its effectiveness from days three to ten post-application. This study also defined direct and secondary pesticide distributions to assess how particle size influences insecticidal activity in the field. The results showed that MC-S's excellent initial activity was due to its wider distribution on organisms' surfaces, greater adherence to pests, and increased resistance to rain washing. MC-L exhibited superior long-term activity due to its light stability, which caused the shell to crack slowly and release phoxim, when exposed to light. Larger MCs increased

the pesticide intake by insects and their movement within their digestive systems. Consequently, increasing MC size can enhance pesticide utilization, if a chemical group responsive to alkaline conditions is integrated into the capsule shell. It was observed that by adjusting particle size, the transfer and release behavior of pesticide from MCs can be regulated in the field.<sup>78</sup>

**3.1.1 Nanoscale polymeric particles (size < 100 nm).** It is known that polymeric nanoparticles have an immense surface area relative to their volume, which enhances their reactivity and ability to penetrate plant tissues. Polymeric nanoparticles are particularly effective for delivering genetic materials and herbicides in a sustainable fashion, if suitably designed. Shan *et al.* demonstrated the fabrication of a UV responsive biodegradable polymeric nanoparticle based spray composed of polyethylene glycol (PEG) based materials for 2,4-dichlorophenoxyacetic acid (2,4-D) delivery (Fig. 3). Even with a loading efficiency and loading content of 16.35% and 5.17%, respectively, the herbicidal efficiency of 2,4-D-loaded nanoparticles was comparable to that of free 2,4-D, effectively inhibiting the growth of *A. thaliana* while the polymer itself had minimal impact on plant health.<sup>68</sup>

A study by Wang *et al.* investigated the utilization of nano-delivery methods for avermectin (Av) with regulated particle sizes, showcasing enhanced controllable release, photostability, and biological activity. Reduced particle sizes led to higher rates of Av release and enhanced biological activity because of greater surface area exposure. These nano-delivery methods exhibited superior penetration and a more gradual and regulated release on target crops in comparison to traditional microcapsules. In addition, they demonstrated excellent storage stability and

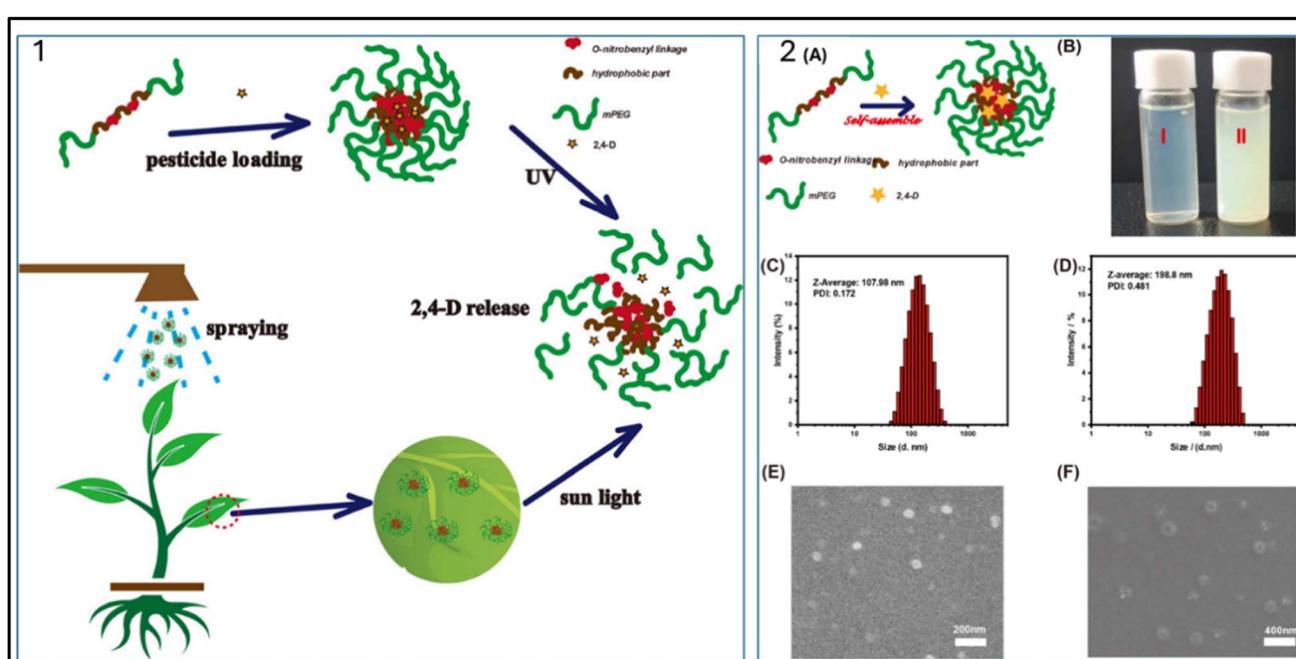


Fig. 3 (1) Application of UV-responsive nanoparticles for 2,4-D release and (2) (A) self-assembly of dextran and cellulose to form nanoparticles, (B) formulation of blank and loaded nanoparticles respectively, (C) and (D) size distribution of nanoparticles and (E) and (F) SEM images of blank and loaded nanoparticles, respectively.<sup>68</sup>



improved effectiveness, which might potentially lead to a decrease in the need for frequent pesticide application.<sup>79</sup>

In another study conducted by Carvalho *et al.*, they developed zein nanoparticles loaded with the herbicide atrazine, to demonstrate their high efficiency in pre-emergence weed control. The nano-formulation proved effective against the target weed (*Brassica juncea*) at a dose 80 times lower than recommended, without harming the crop species (*Zea mays*). Encapsulation of atrazine in nanoparticles did not increase its mobility in the soil, indicating a minimized environmental impact. The nanoherbicide remained in the upper soil layers, effectively targeting the seed bank. The results of the study showed that the nanoparticles were absorbed and accumulated in the roots of both target and non-target plants, with limited transport to the shoots.<sup>80</sup>

### 3.1.2 Microscale polymeric particles (size < 1000 $\mu\text{m}$ ).

These are typically used for macro-encapsulation and are visible to the naked eye. Generally, an inverse relationship is observed between particle size and the rate of agrochemical release, *i.e.*, larger particles exhibit slower release rates due to the reduced surface area. In a study, Metazachlor was encapsulated within micro- and sub-microparticles of low molecular weight PLA, and its release into the aquatic environment was examined. Through the oil-in-water solvent evaporation technique, three particle series (S, M, and L) with varying sizes (ranging from 0.6 to 8 microns) with different concentrations of active ingredient (5–30% w/w) were fabricated, using gelatin (biodegradable) as the surfactant. An encapsulation efficiency of up to 60% was achieved, with lower efficiencies noted for smaller particles. The percentage of herbicide released from the particles over a period of 30 days was studied. As anticipated, the release rate for particles with lower herbicide loadings was less than for the bigger ones. This behavior was due to diffusion-regulated release from larger particles having a reduced surface area, while the smaller particles displayed kinetics profoundly impacted by an initial rapid release due to the increased surface area.<sup>81</sup>

**3.1.3 Beads (size > 1000  $\mu\text{m}$ ).** In agricultural practices, beads are often used for the slow release of nutrients or

chemicals for years. Mun *et al.* developed alginate beads loaded with pacllobutrazol (PBZ) encapsulated montmorillonite-polycaprolactone microparticles (MPs) and found that the release of PBZ was consistent and aligned with multi-year rainfall patterns (Fig. 4). The alginate serves as a stable matrix, while the engineered microparticles provide controlled, sustained release of PBZ to inhibit growth over several seasons.<sup>64</sup>

In summary, the size of polymeric particles plays a critical role in determining their application efficiency and biological performance in agricultural systems. Nanoscale particles (<100 nm) exhibit enhanced reactivity, penetration, and targeted delivery capabilities, making them ideal for applications requiring precision and controlled release, as demonstrated by nanoherbicide and nanopesticide formulations.<sup>79</sup> Microscale particles (<1000  $\mu\text{m}$ ) offer a balance between sustained release and scalability, particularly for applications like soil-targeted herbicides. Beads (>1000  $\mu\text{m}$ ), with their ability to provide multi-year-controlled release, are well-suited for long-term nutrient delivery and crop growth regulation. The choice of particle size must therefore align with the specific agricultural objective, ensuring optimal efficacy while minimizing environmental impact.

## 3.2 Shape

Apart from size, the shape of polymeric particles too has a significant impact on their action in the agricultural field.

**3.2.1 Isotropic spherical shape.** The most common shape of polymeric particles is spherical. Sometimes, spherical particles have a lower surface area as compared to other shapes, which can help in slow degradation and controlled release.<sup>82</sup> They are easier to manufacture with consistency and often exhibit favorable flow properties.<sup>51</sup> In a study, it was found that spherical particles of cellulose acetate butyrate (CAB) and cellulose acetate propionate (CAP) provide a more controlled and sustained release as compared to non-spherical particles because of the uniformity of the spheres (Fig. 5).<sup>83</sup>

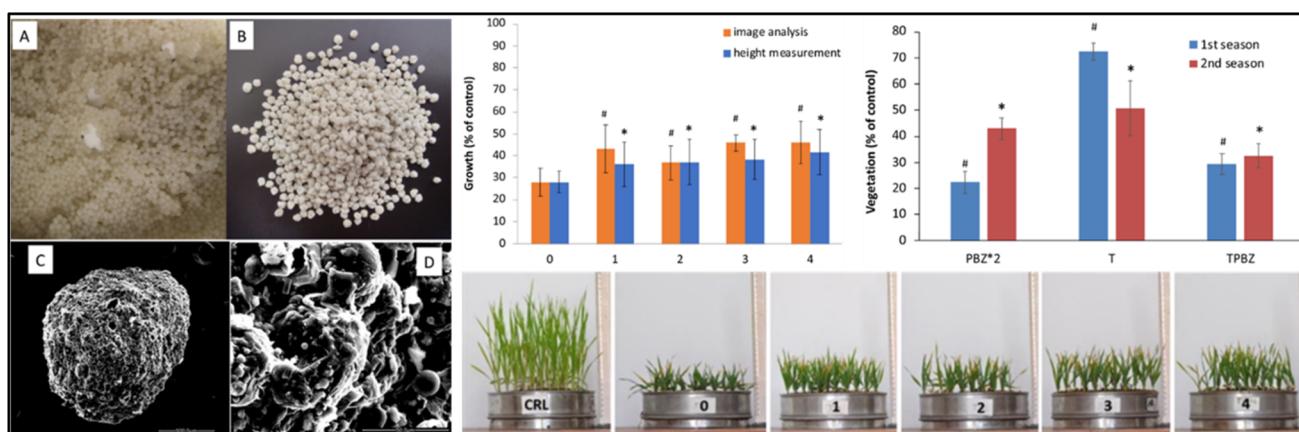


Fig. 4 The impact of alginate/clay beads with PCL-PBZ microparticles on oatmeal growth, showing the beads pre- and post-lyophilization (A and B), SEM details (C and D), vegetation growth in treated soil over up to four rainy seasons, and sprout development on sieves after water exposure simulating up to five rainy seasons.<sup>64</sup>



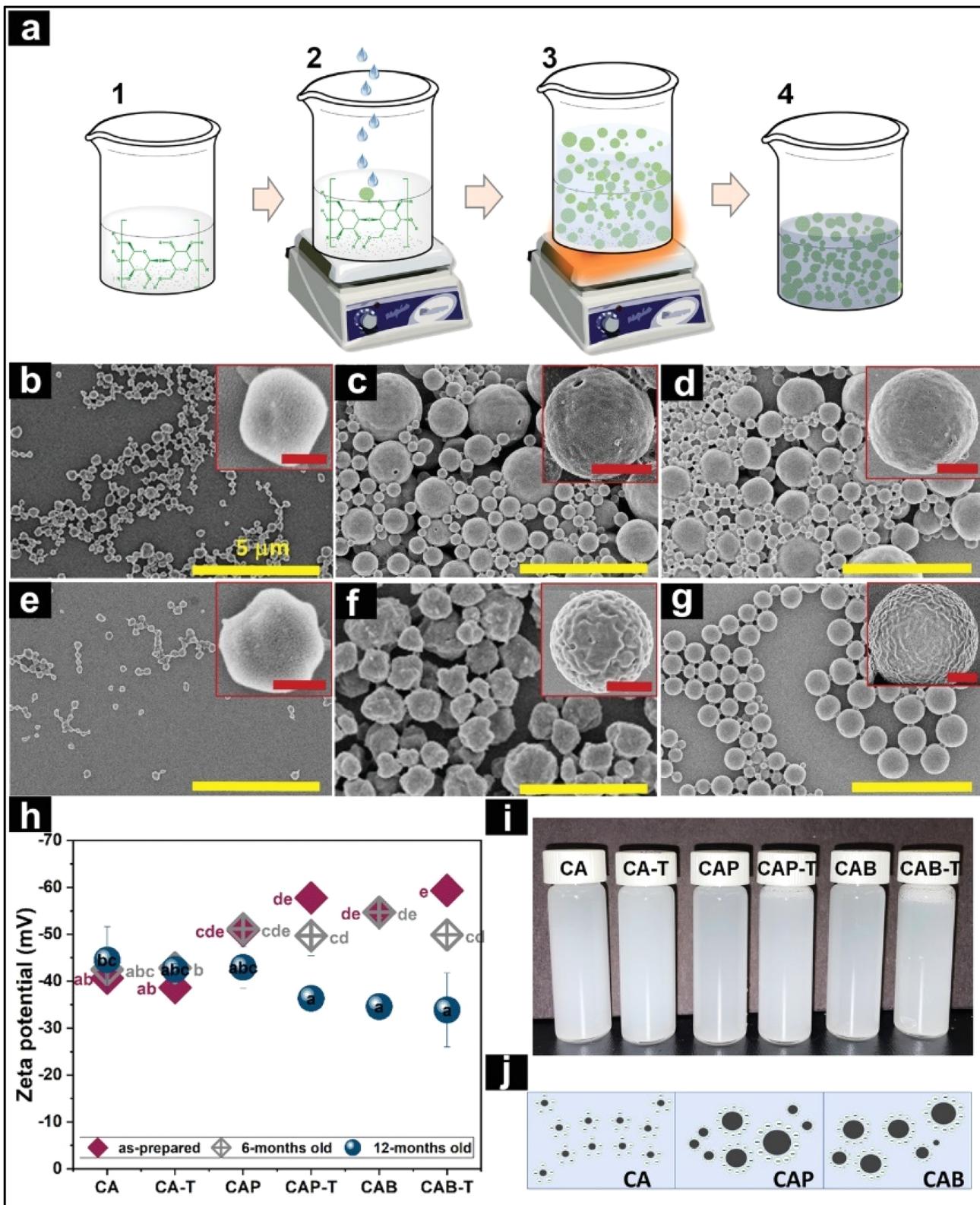


Fig. 5 (a) Fabrication of cellulose based microparticles, (b–g) SEM images of various cellulose based microparticle systems, (h) zeta potential of different systems, (i) aqueous dispersion of different microparticle systems, and (j) schematic representation to depict the dispersion stability of CA (cellulose acetate), CAP, and CAB particles.<sup>83</sup> Reused with permission from the publisher.

**3.2.2 Anisotropic shapes.** These are less commonly designed and developed but can result from certain synthesis processes. The irregularities affect the release profile and physical properties of the particles.<sup>84</sup> Pirzada *et al.* demonstrated that the shape of particles is crucial when using them for foliar applications. They designed anisotropic shaped cellulose-based nanoparticles by varying the substituent groups in cellulose esters to alter the particle shape, size and morphology. These particles have demonstrated excellent rain fastness that resulted in very low surface loss after stimulating a  $>50$  mm h<sup>-1</sup> rainfall test.<sup>83</sup>

### 3.3 Morphologies

The surface morphology of the polymeric particles predominantly governs their action in delivering agrochemicals, as discussed below.

**3.3.1 Solid particles.** These are completely solid particles, which contain the active ingredients uniformly distributed throughout the polymer matrix. Their design effectively prevents premature degradation of the active ingredients.<sup>85,86</sup> The release of the active ingredient occurs primarily through diffusion and *via* the gradual degradation of the polymer. For instance, Mummasani *et al.* studied calcium cross-linked xanthan gum-alginate based polymeric solid particles incorporated with diclosulam for prolonged weed control in irrigated upland ecosystems. This system offered both burst and controlled release of diclosulam and showed synchronized herbicide release with weed suppression, thereby enhancing weed management in crop fields.<sup>87</sup>

**3.3.2 Porous particles.** Particles, which have a porous structure, can absorb and trap large amounts of active ingredients due to their high surface area. Porous particles release their contents slowly as the polymer degrades or in response to external stimuli. Kobylinska *et al.* fabricated stereo-complexed porous particles made from enantiomeric polylactides such as poly D-lactide (PDLA) and poly L-lactide (PLLA). Enantiomeric polylactides were synthesized using ring-opening polymerization and used to create quercetin-loaded porous microparticles *via* spontaneous precipitation in an organic solvent. These biodegradable porous microparticles (size  $\sim 2$  to 6  $\mu\text{m}$ ) were designed for sustained quercetin release and slow degradation to improve plant growth under high salinity conditions. The quercetin-loaded porous particles released the active steadily in both water and 0.9 M NaCl solutions. Quercetin is a flavonoid having antioxidant properties that allow plant growth by enhancing plant tolerance against biotic and abiotic stresses. As a result, they significantly improved the growth of green peas under salinity stress, increased relative water content by 15–20%, enhanced phenolic content for better antioxidant properties, and boosted chlorophyll content to maintain leaf color and photosynthetic efficiency. They demonstrated the potential of using biocompatible and biodegradable porous carriers for improved crop production under adverse conditions.<sup>88</sup>

**3.3.3 Capsules or core–shell structures.** These feature a core that contains the active ingredient, surrounded by

a polymer shell. The shell can be engineered to degrade under specific environmental conditions, such as changes in pH, temperature, or moisture, allowing for triggered release at targeted locations.<sup>89</sup> Xu *et al.* developed biopolymer-based multi-stimuli responsive core–shell nanostructures for smart agro-chemical delivery<sup>90</sup> (Fig. 6). Spherical core–shell nanostructures, loaded with NPK macronutrients and CuSO<sub>4</sub>, were fabricated using the coaxial electrospraying technique (average diameter  $\sim 160$  nm). The pH and enzyme responsive release of these nanostructures extended up to seven days in aqueous media. The efficacy of the stimuli-responsive nanostructures was also assessed in greenhouse experiments conducted in soil, using soybean and wheat as the subjects. The focus was on evaluating the efficiency of photosynthesis and linear electron flow (LEF), both of which are crucial for the growth and well-being of seedlings.

The findings validated the specificity of the plants; in the case of soybean, the nanostructures led to a 34.3% increase in relative chlorophyll content and a 41.2% increase in the value of photosystem 1 (PS1) centers in photosystem I, as compared to the ionic control with an identical quantity of agrochemicals. The nanostructures resulted in a 37.6% increase in the LEF (linear electron flow) value of wheat as compared to ionic agrochemicals administered at a concentration four times higher. This shows that the responsive core–shell nanostructure is an efficient method for delivering agrochemicals with precision while limiting the amount needed. Moreover, the presence of the nanostructure amendment led to a substantial rise in the zinc (Zn) and sodium (Na) levels in the leaves of four-week-old soybean seedlings. Therefore, the created nanostructures have the potential to improve the accumulation of additional vital micronutrients, indicating a feasible approach for biofortification.<sup>90</sup>

**3.3.4 Multilayer particles.** These are composed of multiple concentric layers of different polymers, each of which may contain different active ingredients or degrade at different rates, providing sequential release.<sup>91,92</sup> Zhang *et al.* engineered multilayer polymeric particles loaded with lambda-cyhalothrin (LC) *via* electrostatic self-assembly of sodium lignosulphonate (SL) and dodecyl dimethyl benzyl ammonium chloride (DDBAC) followed by iron mineralization (Fig. 7). Iron mineralization played a crucial role in their stabilization, and it significantly extended the half-life of LC under UV irradiation by 4.4 times. The LC-loaded nanocarriers (LC@SL/DDBAC/Fe) demonstrated dual responsive release behavior and showed approximately 39% higher mortality rates against *Agrotis ipsilon*.<sup>93</sup>

The shape and morphology of polymeric particles significantly influence their performance in agricultural applications, dictating the release profiles, environmental stability, and overall efficacy of the active ingredients. Spherical particles, with their ease of manufacture and uniformity, are well-suited for controlled and sustained release applications, while anisotropic shapes demonstrate superior adhesion properties, particularly for foliar applications.

Morphological innovations, such as porous structures, core–shell designs, and multilayer particles, offer advanced



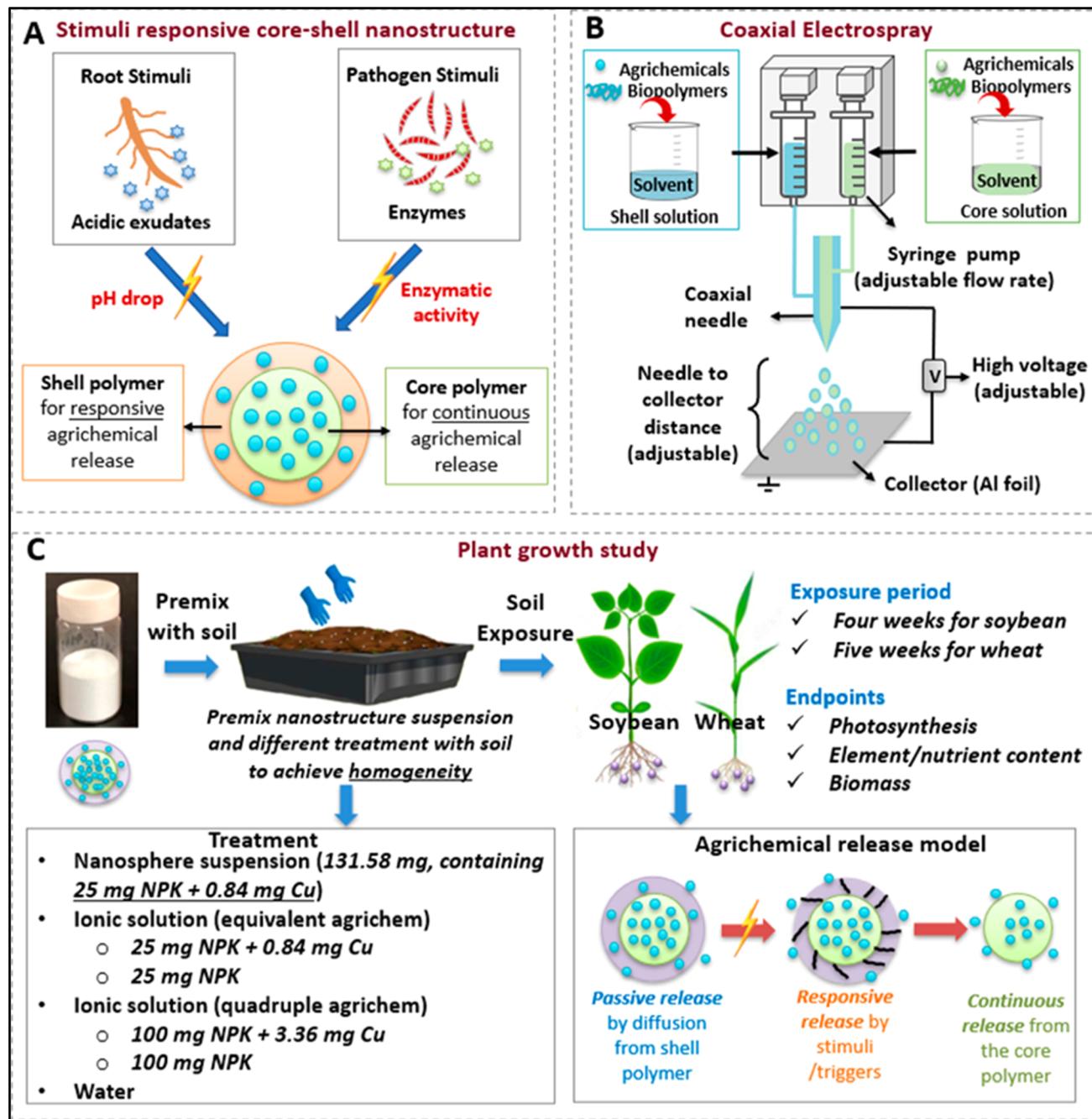


Fig. 6 (A) pH and enzyme responsive activity of nanoparticles, (B) fabrication of core–shell nanoparticles using a coaxial needle setup, and (C) soil study and results of treatment with nanoparticles.<sup>90</sup> Reused with permission from the publisher.

capabilities for precision delivery and responsiveness to environmental stimuli. By tailoring shape and morphology to specific agricultural needs, these polymeric particles hold immense potential to enhance agrochemical efficiency, reduce environmental impact, and improve crop resilience under varying conditions. However, the efficacy of biodegradable polymeric particles in agricultural applications depends largely on the efficiency and precision of their fabrication techniques. Some common fabrication techniques of biodegradable polymeric particles are discussed next.

#### 4. Fabrication techniques of biodegradable polymeric particles

Several methods are employed to produce biodegradable polymeric particles as per the requirements based on the end application. These include scalable and customizable production techniques, materials' versatility with diverse sources and functionalization capabilities, and economic benefits from cost-effective production, regulatory compliance, and improved marketability.

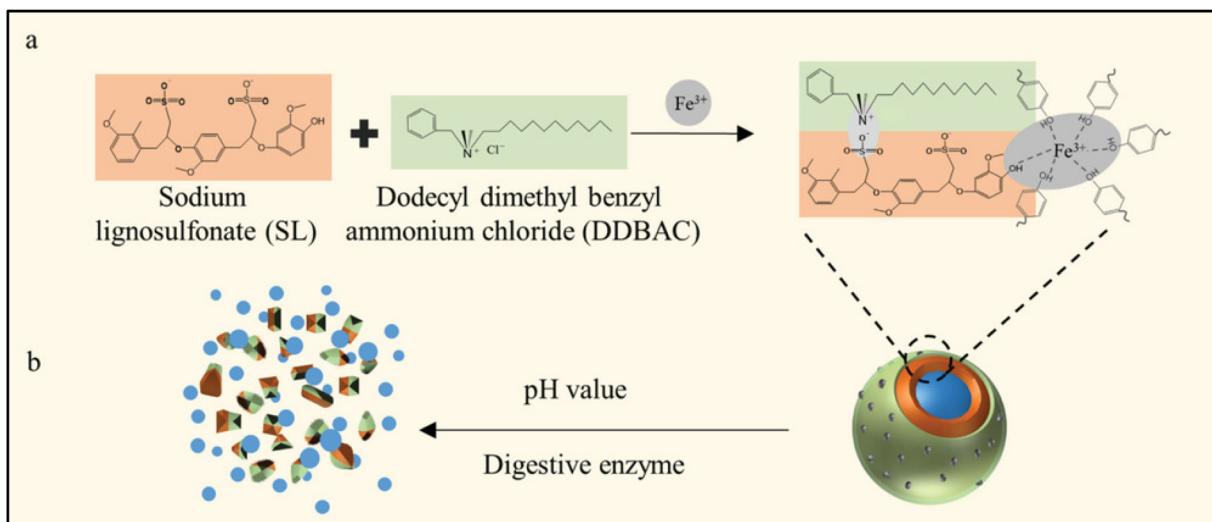


Fig. 7 (a) Synthesis of multilayer microparticles. (b) Degradation of microparticles under the influence of pH change and enzymes.<sup>93</sup> Reused with permission from the publisher.

#### 4.1 Emulsion solvent evaporation method

This widely utilized approach involves the creation of an emulsion, either oil-in-water or water-in-oil, depending on the nature of agrochemicals and polymers used. The polymer is usually dissolved in the organic phase (oil), while the aqueous phase contains a stabilizer. Through solvent evaporation, the organic solvent is removed, leading to the solidification of the polymer and the formation of particles (Fig. 8).<sup>3,66,94-97</sup> Taverna *et al.* investigated the potential of PLA/lignin based microparticles for encapsulating azadirachtin (AZD) (hydrophilic pesticide) and protecting it from photodegradation. The encapsulation efficiency of microparticles with a 55:45 ratio was 23.25%, demonstrating that the higher lignin content enhances the bio-pesticide's encapsulation efficiency. Release assays in water indicated a slower release rate for formulations with higher PLA content. Moreover, AZD showed greater

photodegradation as a free compound as compared to when encapsulated in microparticles, indicating the enhanced stability of actives in the encapsulated form.<sup>94</sup>

Lopes *et al.* developed an emulsion/cross-linking method to enclose *Bacillus megaterium* in starch/PVA microparticles. STMP (trisodium trimetaphosphate) was used as a cross-linking agent. Both types of microparticles retained high cell viability after encapsulation, with controlled release profiles. The bacteria that were enclosed did a better job of retaining their cell viability under heat and fungicide stress than free bacteria. The efficacy of particles was well preserved during storage.<sup>49</sup>

#### 4.2 Anti-solvent nanoprecipitation

This technique involves the precipitation of a solute from a solution using an antisolvent in which the solute is insoluble. The process begins with the solute, such as a drug or polymer,

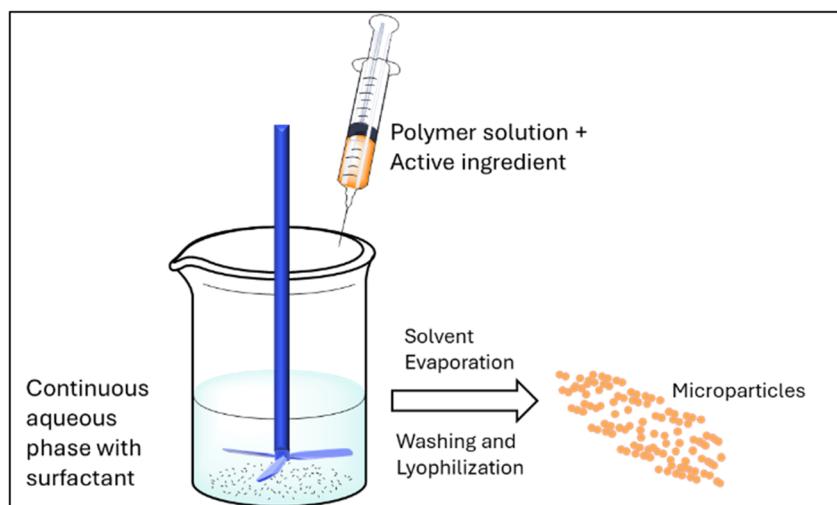


Fig. 8 Illustration of the solvent evaporation technique for fabrication of active ingredient-loaded microparticles.



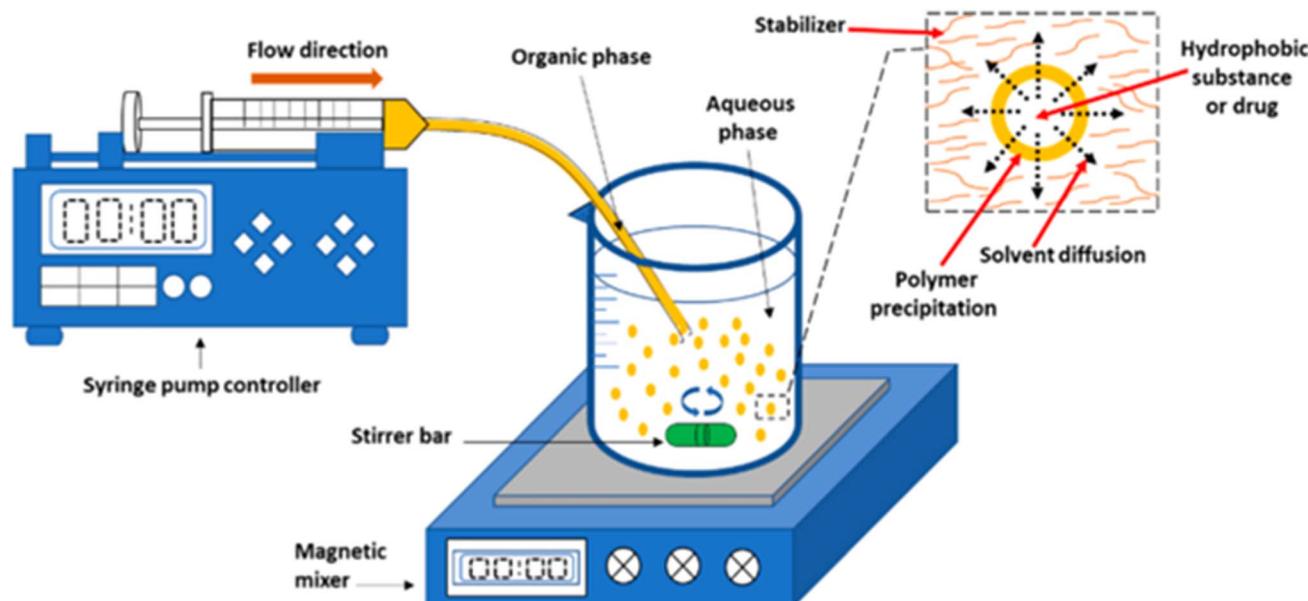


Fig. 9 Schematic representation of the anti-solvent nanoprecipitation method.<sup>99</sup> Adapted from an open-access article distributed under the terms of the Creative Commons Attribution License (CC BY).

dissolved in a solvent like ethanol or acetone. This solute solution is then rapidly introduced into an antisolvent, typically water or an aqueous solution, under vigorous stirring. The rapid mixing creates a supersaturated environment, causing the solute to precipitate out of the solution as small nuclei. These nuclei grow into nanoparticles as additional solute molecules aggregate onto them. To prevent these nanoparticles from clustering together, stabilizers or surfactants are added; these molecules adsorb onto the nanoparticles' surface, providing a barrier against aggregation. The sudden change in the environment triggers the rapid precipitation of the polymer into nanoparticles (Fig. 9).<sup>96,98</sup> This technique offers good control over particle size by adjusting polymer concentration and mixing ratios. Encapsulation efficiency for hydrophobic agents may

be limited; scaling up to produce large quantities can be challenging.<sup>80</sup> Researchers in Poland used this method to fabricate particles with porous architectures and dimensions ranging from 2 to 6  $\mu\text{m}$ . Subsequently, the efficacy of the quercetin-loaded microparticles in fertilizing *Pisum sativum* L. (green peas) was assessed. The study found that using biocompatible and biodegradable carriers that are loaded with flavonoids (hydrophobic) improves plant growth.<sup>88</sup>

#### 4.3 Ionotropic gelation

This technique is used to synthesize nanoparticles, particularly those based on polysaccharides. This method is based on an electrostatic interaction between oppositely charged types that

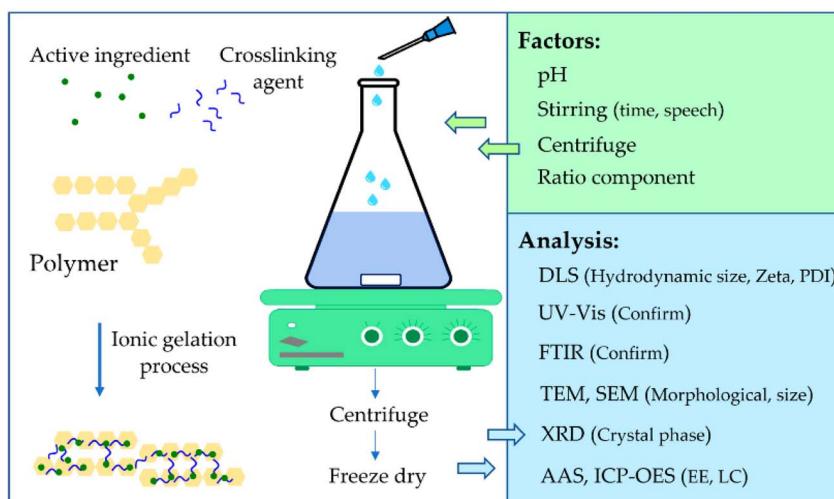


Fig. 10 Illustration of the ionotropic gelation method.<sup>102</sup> Adapted from an open-access article distributed under the terms of the Creative Commons Attribution License (CC BY).



contain at least one polymer under mechanical stirring conditions (Fig. 10).<sup>100</sup> Chitosan, a polysaccharide obtained from the shells of crustaceans, is often used in this method. The process involves dissolving polysaccharides such as alginate, gellan, and pectin in water or in a weakly acidic medium (for chitosan). The ionotropic gelation method can also be used with chitosan and negatively charged polyanion groups of sodium tripolyphosphate (TPP) to create chitosan nanoparticles.<sup>101</sup> The chitosan/S-nitrosoglutathione nanoparticles (CS-GSNONPs) exhibited prolonged and controlled release of nitric oxide (NO) gas, in contrast to free GSNO. This suggests that the inclusion of GSNO in CSNPs safeguards the donor of NO from rapid degradation and enables optimal release of NO. The resilience of soybean plants to drought was significantly improved by the application of CS-GSNONPs, evidenced by the substantial increase in plant height, biomass, root length, root volume, root surface area, and the number of root tips, forks, and nodules. Follow-up analyses revealed a significant reduction in electrolyte leakage, an increase in proline content, heightened catalase and ascorbate peroxidase activities, and lower levels of malondialdehyde (MDA) and hydrogen peroxide ( $H_2O_2$ ) after treatment with 50  $\mu M$  CS-GSNONPs during drought stress. Further investigations using quantitative real-time PCR indicated that CS-GSNONPs alleviated drought-induced stress by controlling the expression of drought stress marker genes, such as GmDREB1a, GmP5CS, and GmDEFENSIN, as well as NO-related genes GmGSNOR1 and GmNOX1.<sup>101</sup>

Zheng *et al.* fabricated Ca-alginate/poly(*N*-isopropylacrylamide)@polydopamine (Ca-alginate/PNIPAm@PDA) microparticles designed for controlled agrochemical release. These multi-responsive microspheres respond to pH, temperature, and sunlight, making them ideal for agricultural applications. The resulting microspheres were strengthened by a semi-interpenetrating network, composed of a hybrid combination of physically cross-linked Ca-alginate and chemically cross-linked long-chain PNIPAm, which is then coated with PDA. The composite microspheres exhibit sensitivity to sunlight because of the remarkable photothermal conversion of the PDA shell. The Ca-alginate chain, which is sensitive to changes in pH, and the PNIPAm chain, which is sensitive to changes in temperature, were responsible for the effects of the external environment on their water absorbency behavior.<sup>103</sup>

#### 4.4 Spray drying

In this method, a polymer solution is atomized into a hot drying chamber. Rapid solvent evaporation results in the formation of dry particles. This technique is easily scalable and suitable for continuous production on a large scale (Fig. 11). It provides good control over particle size and morphology.<sup>72,104</sup> Perez *et al.* developed a method for encapsulating the photosensitive spinosad (SP) (hydrophobic) into chitosan (CH) and sodium lignosulfonate (SL) microparticles. The microparticles were acquired through the process of spray drying and were assessed for their shape using scanning electron microscopy (SEM) and particle size. The *in vitro* release assays exhibited an initial rapid release of the bioinsecticide, which was followed by a gradual

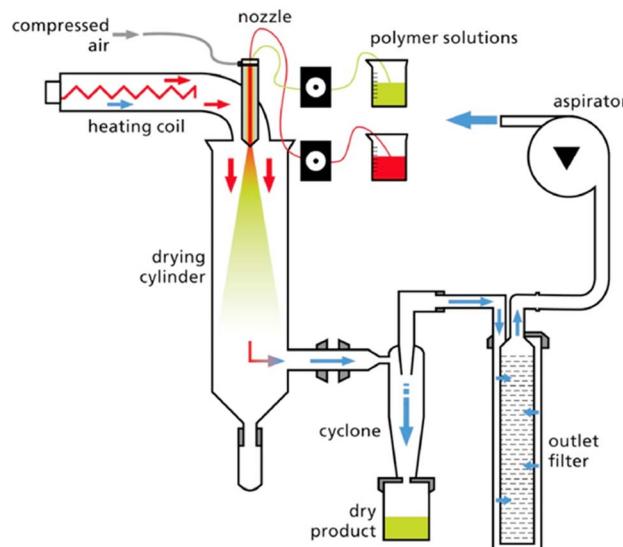


Fig. 11 Schematic of the spray drying process.<sup>105</sup> Reused with permission from the author.

and sustained release. The findings of this study indicate that the bioinsecticide carrier system, made from natural polymeric materials, has excellent resistance to photodegradation and effectively releases insecticide. This system may be employed as a viable approach to mitigate the adverse environmental effects associated with agronomic activities.<sup>72</sup>

Saberi-Rise and Moradi-Pour fabricated chitosan-based microcapsules loaded with bacterial inoculants using the spray drying method. They found that the quantity of *Streptomyces fulvissimus* Uts22 bacteria in chitosan-gellan gum microcapsules, generated using this technique, was around 108 CFU  $g^{-1}$  after being stored for a duration of 2 months.<sup>106</sup>

The fabrication techniques for biodegradable polymeric particles play a pivotal role in tailoring their properties for diverse agricultural applications. Methods like emulsion solvent evaporation and spray drying offer scalability and versatility, making them suitable for large-scale production with controlled particle sizes and morphologies. Advanced techniques like anti-solvent nanoprecipitation and ionotropic gelation enable the design of specialized nanoparticles with enhanced delivery efficiency and environmental responsiveness. These fabrication approaches not only ensure the stability and efficacy of the active ingredients but also contribute to sustainable agricultural practices by minimizing environmental impact. The choice of the fabrication method depends on the specific application requirements, such as particle size, release profile, and compatibility with active ingredients, highlighting the importance of method selection in optimizing performance and scalability for agricultural innovations (Tables 1 and 2).

## 5. Tailoring properties of polymeric particles for desired applications

The effectiveness of biodegradable polymeric particles in agriculture hinges on a delicate balance between their material



Table 1 Summary of various techniques used for fabrication of polymeric micro/nanoparticles

Technique	Advantages	Limitations	Scalability	Particle size control	Encapsulation efficiency	References
Emulsion/solvent evaporation	Simple and versatile, good control over particle size, allows encapsulation of various agents	Moderate encapsulation efficiency, potential for residual organic solvents, difficulty in achieving very small particle sizes	Moderate	Good	High	49 and 107
Spray drying	Scalable and continuous process, suitable for large-scale production, good control over particle size and morphology	High temperatures may degrade sensitive biomolecules, potential for irregular encapsulation efficiency	High	Good	Moderate	72 and 108
Antisolvent nano-precipitation	Simple and efficient method for producing small nanoparticles, good control over particle size through adjustments in polymer concentration and mixing ratios	Limited encapsulation efficiency for hydrophobic agents, potential challenges in scaling up production for large quantities	Moderate	Good	Low	93
Ionotropic gelation	Simple and biocompatible, a wide range of polysaccharides can be used, excellent encapsulation of biomolecules	Limited control over size and morphology (especially after drying), particle properties can be influenced by ionic strength	High	Moderate	Moderate-high	109

properties and the specific application for which they have been designed. Controlling the size, shape, and surface topography of the particles influences their uptake by plants, interaction with soil, and release characteristics. Herein, we delve into the key properties and characteristics that influence the suitability of these particles for various agricultural uses.

### 5.1 Physical properties

A critical characteristic of a particle is the rate at which the encapsulated agent (nutrients, pesticides, etc.) is released from the particle. Ideally, the release profile should be tailored in such a manner that it fulfills the specific needs of the plant at different stages of its growth cycle.<sup>64</sup> Factors like polymer type, particle size, and surface modifications can be used to control the release rate. Varona *et al.* fabricated particles through PGSS (particles from gas-saturated solutions) drying, which typically exhibited two distinct morphologies: spherical particles and small irregularly shaped crystals and needles.<sup>110</sup> The PGSS and PGSS-drying methods differed significantly in their encapsulation processes, materials used, operating conditions, and particle characteristics. PGSS mixed molten polyethylene glycol (PEG) and essential oil with CO<sub>2</sub> under high pressure, rapidly expanding the mixture to form microcapsules. In contrast, PGSS-drying employed an oil-in-water emulsion with *n*-octenyl succinic (OSA)-starch as a surfactant, mixed with CO<sub>2</sub>, and then expanded to remove water and form microcapsules. While PGSS used PEG as the encapsulating material, PGSS-drying uses OSA-modified starches. Operating conditions for PGSS were milder, as it did not require water removal, unlike PGSS-drying, which involved higher temperatures and pressures for water removal.

As a result, PGSS produced spherical particles with higher encapsulation efficiency (14–66%), whereas PGSS-drying resulted in both spherical and needle-like particles with lower encapsulation efficiency (6–52%). These differences affected the efficiency, particle size, and morphology of the encapsulated essential oils. Overall findings from the emulsion study suggest that particle morphology, size distribution, and encapsulation efficiency are influenced not only by the precipitation process, but also by the solvent evaporation process. Consequently, it can be inferred that the PGSS-drying technique has its own limitations, particularly when needle morphology is formed, which is unsuitable for achieving controlled oil release. In contrast, PGSS yielded dispersed spherical particles with some degree of agglomeration. This, coupled with the higher encapsulation efficiency observed in PEG encapsulation *via* PGSS, leads to the conclusion that among the two processes investigated, PGSS is better suited for lavandin type essential oil encapsulation.<sup>110</sup>

Next-generation particles are being developed to incorporate stimuli-responsive features. These particles can release their cargo in response to environmental cues like temperature, pH, or moisture levels. The targeted release ensures that the encapsulated agent is delivered, when it is most needed by the plant, minimizing waste and maximizing efficiency. A novel, scalable, and environmentally friendly approach was developed for creating multi-stimuli responsive nanostructures from biopolymers, aimed at delivering agrochemicals effectively. Using a coaxial electrospray method, these core/shell nanostructures were fabricated with meticulous parameter analysis and optimization, resulting in spherical structures around



Table 2 Applications of BPPs in agriculture

Polymer	Technique	Particle morphology	Active ingredient	Effect	References
Alginate + starch	Ionotropic gelation	Microbeads	L-tryptophan and <i>B. pumilus</i> (bacteria)	Plant growth promoter by accelerating auxin production and enhancing the drought tolerance of plants	76
Cellulose nanofibrils (CNFs)	Spray drying	Microcapsules and microspheres (spherical)	KNO <sub>3</sub>	Enhanced nutrient uptake and controlled release of the fertilizer for improved plant growth efficiency	104
Chitosan	Ionotropic gelation	Nanoparticles	S-Nitrosoglutathione	Enhanced root development under drought stress conditions	101
Chitosan/sodium lignosulfonate	Spray drying	Microparticles	Spinosad	Sustained release of photosensitive insecticides	72
Chitosan/gum Arabic	Emulsion and ionotropic gelation	Nanoparticles	Geraniol	Modulated release of geraniol to attract whiteflies (pest management) and UV protection of active material	155
Cellulose-alginate complex	Ionotropic gelation	Beads	Imazethapyr	Sustained release of the herbicide in the field	156
Lignin/PLA blend	Solvent evaporation method	Microparticles	Azadirachtin	Tunable particles for sustained release of biopesticides	94
Polylactic acid (PLA)	Solvent evaporation method	Microparticles	Di( <i>t</i> -butanol) dithiophosphate phenethylamine	Sustained release of H <sub>2</sub> S for enhanced growth of radish plants	95
Polylactic acid (PLA)	Solvent evaporation method	Microparticles	Buprofezin	Protection against insects and pests like mealybugs, whiteflies and leafhoppers	66
Poly(salicylic acid)	Nanoprecipitation	Nanoparticles (spherical)	Acifluorfen	Enhanced herbicidal activity and lower environmental pollution	157
Poly( $\epsilon$ -caprolactone) (PCL)	Solvent evaporation method	Microparticles	Pacllobutrazol	Plant growth retardation	64
Polydopamine (PDA)	Self-assembly	Microcapsules (spherical)	Pyraclostrobin	Controlled release of the pesticide, photostability under UV light	158
Polyhydroxyalkanoates (PHAs)–PHB and PHBV	Solvent evaporation method	Microparticles	Metribuzin, tribenuron-methyl, fenoxaprop- <i>P</i> -ethyl	Sustained release of herbicides studied on the <i>Elsholtzia ciliata</i> plant	96
Zein	Nanoprecipitation	Nanoparticles	Atrazine	Targeted and sustained release of the herbicide	159

160 nm in diameter. These structures demonstrated responsiveness to pH and enzymes, as evidenced by the release kinetics of model agrichemicals (Fig. 12). The core and shell compositions of the nanoparticles were carefully selected to optimize their agricultural performance. The core primarily consists of polycaprolactone (PCL), chitosan, and cellulose acetate, along with a higher concentration of agrichemicals like CuSO<sub>4</sub> and NPK fertilizer. PCL was chosen for its biodegradability and ability to improve the processing stability and morphology of the nanostructures. Chitosan provides pH-responsive properties, transitioning between soluble and insoluble forms around pH 6.0–6.5, while cellulose acetate adds hydrophobicity to control the release of agrichemicals. The shell includes starch, PCL, chitosan, cellulose acetate, and zein, with varying concentrations of CuSO<sub>4</sub> and NPK depending on the desired release rate. Starch and zein were selected for their

enzyme responsiveness, as they can be degraded by soil fungi. The shell's composition was adjusted to be more hydrophilic or hydrophobic to achieve different release profiles, ensuring efficient delivery and utilization of nutrients while minimizing the environmental impact. Field trials with soybean and wheat plants indicated that these responsive nanostructures outperformed conventional agrichemicals, even when applied at higher concentrations. Furthermore, soybean seedlings treated with nanostructures showed significant increases in zinc and sodium contents in their leaves, highlighting the precision and efficacy of agrichemical delivery.<sup>90</sup>

Responsive microgel particles based on octyl-functionalized alginate were fabricated to control the release of agrochemicals and capture heavy metal ions in agriculture. These microgel particles demonstrated efficient loading of the hydrophobic herbicide such as diuron, with its release controlled by



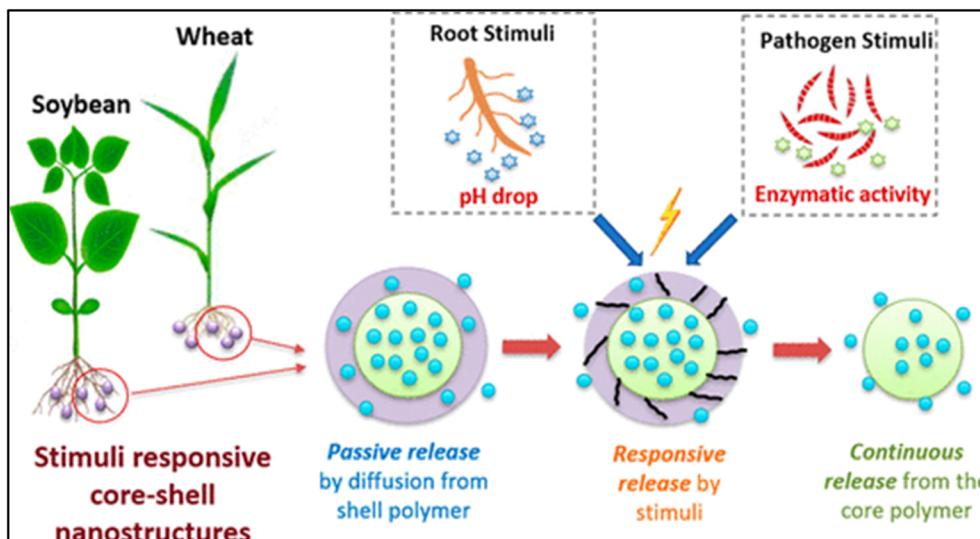


Fig. 12 Stimuli responsive nanoparticles.<sup>90</sup>

adjusting the glutathione (GSH) levels and pH of the medium. Extended release of diuron was achieved, with approximately 100% released after 380 h in 2 mM GSH and about 72% released after 240 h at pH 5. These microgel particles were found to be non-toxic to HEK293T cells up to concentrations of  $150 \mu\text{g mL}^{-1}$ . Moreover, GSH-reduced microgels were also effective in capturing  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  heavy metal ions.<sup>69</sup>

## 5.2 Surface modifications

The surface properties influence the release behavior of the encapsulated agent (nutrients, pesticides, *etc.*) from the particle. Particles with a hydrophilic surface readily absorb water. This promotes water diffusion into the particle matrix, facilitating the dissolution and release of the encapsulated agent.<sup>111</sup> This is advantageous for delivering water-soluble nutrients or beneficial microbes, while those with a hydrophobic surface will repel water. The hydrophobic surface hinders water diffusion into the particle and slows down the release of the encapsulated agent. This can be beneficial for hydrophobic pesticides or herbicides, as it prevents premature release and potential environmental contamination.<sup>66</sup> Modifying the surface properties of the particle can influence its interaction with other molecules and its behavior in the soil environment. For instance, hydrophilic surfaces promote water absorption and improve interaction with plant roots, while hydrophobic surfaces can be used for controlled release of hydrophobic pesticides.<sup>112</sup> Specific functional groups can be attached to the particle surface to enhance targeted delivery.<sup>113,114</sup> These groups can bind to receptors on plant roots or specific types of soil particles, ensuring that the particles reach the desired location for optimal effectiveness.<sup>115</sup> Nanoparticles, which are responsive to plant phloem's elevated pH, were engineered to create a targeted delivery system for plants. Photosystem 1 (PS1) is one of the two protein complexes embedded in the thylakoid membrane within chloroplasts of plant cells. It is responsible for light capture, electron transfer,

proton pumping and production of NADPH (Nicotinamide Adenine Dinucleotide Phosphate Hydrogen) molecules. Amphiphilic copolymers derived from PS1 were synthesized by incorporating various amines, allowing for flexible adjustment of the hydrophilic-hydrophobic balance, essential for nanoparticle formation. Modulating the level of incorporation and the conditions of nanoprecipitation emerged as effective strategies for controlling the nanoparticles' size, which could prove advantageous in developing novel delivery systems. These nanoparticles, loaded with a hydrophobic model compound, exhibited controlled release under alkaline conditions, with release rates increasing with higher solution pH and lower degrees of incorporation. Additionally, the toxicity of the polymers on plant tissue was evaluated, revealing minimal toxicity at reasonable polymer concentrations.<sup>116</sup>

## 6. Applications of biodegradable polymeric particles in agriculture

Biodegradable polymeric particles are revolutionizing agriculture by offering a targeted and controlled approach to delivering essential elements to plants and soil. This section delves into the exciting applications of these particles in various agricultural aspects, highlighting their potential for sustainable farming practices.

### 6.1 Controlled release systems for agrochemicals

One of the most promising applications of biodegradable polymeric particles involves the controlled release of agrochemicals like fertilizers, pesticides, and herbicides. Traditional application methods often lead to significant losses due to factors like leaching, volatilization, and runoff. These losses not only reduce efficiency but also contribute to environmental pollution.

Biodegradable polymeric particles act as carriers, encapsulating agrochemicals and releasing them at a controlled rate

over a predetermined period. This targeted delivery offers several advantages:

- Reduced environmental pollution. By minimizing excess uses, these particles significantly reduce the risk of groundwater contamination and soil pollution from agrochemicals.<sup>43</sup>
- Improved nutrient efficiency. Controlled release ensures that nutrients are available to plants throughout their growth cycle, maximizing uptake and minimizing waste.<sup>69,92,117</sup>
- Enhanced efficacy of pesticides/herbicides. Targeted delivery to specific areas or pests improves the effectiveness of these chemicals while reducing the risk of harming beneficial insects and non-target plants.<sup>67,69,118,119</sup>

**6.1.1 Fertilizer delivery.** Particles loaded with essential nutrients like nitrogen, phosphorus, and potassium can be tailored to release slowly, matching the specific needs of a crop at different stages of its growth cycle. This targeted delivery not only improves nutrient uptake efficiency, but also reduces fertilizer runoff into waterways. In this regard, controlled-release fertilizers (CRFs) offer benefits such as enhancing nutrient use efficiency (NUE) and reducing nutrient loss (particularly due to nitrate leaching and the release of nitrous oxides and ammonia), thus aiding in reducing environmental contamination. Additionally, it is feasible to lower fertilizer application rates by up to 30% of the recommended dosage while maintaining equivalent crop yields.<sup>120</sup> This approach can yield economic benefits by conserving labor, time, and energy resources. Controlled-release fertilizers coated with biodegradable polymers are crucial for overall reduction of cost,<sup>121</sup> enhancing marketability, preserving soil fertility, achieving high yields of crops, and addressing climate challenges. It is recognized that utmost 30% of the fertilizer encapsulated in these systems remains unreleased due to differences in the concentration gradient across the polymer coatings.<sup>122</sup> In order to liberate encapsulated fertilizers, it is essential that the polymer coatings degrade entirely after the agrochemicals have been completely discharged in the soil. However, biopolymers like PHAs (polyhydroxy alkanoates) are biodegradable and effective as matrices in controlled-release formulations, but their commercial production from bacteria increases the cost of PC-CRFs' (polymer coated controlled release fertilizers) production.<sup>122,123</sup>

A few researchers at the University of Massachusetts combined biodegradable polymers with urea phosphate to create "smart fertilizers" to promote sustainable agricultural practices. Urea phosphate (UP) is used as a water-soluble fertilizer to treat the deficiency of phosphorus in alkaline soils. Slow diffusion of phosphate through coatings of slow-release fertilizers has been identified as a bottleneck in the supply of nitrogen-phosphorus-potassium (NPK) nutrients. They investigated how the structure of the polymer matrix affects release kinetics using biodegradable polyesters and their copolymers such as poly(hexamethylene succinate) (PHS), PBHS 30/70, and PBHS 70/30 (where 30/70 and 70/30 indicate the w/w composition of butylene succinate and hexamethylene succinate, respectively). Composite materials comprising UP and polyester, manufactured through melt processing, were studied to evaluate UP loading efficiency, as well as the distribution and

dispersion of the phosphate salt within the polymer matrix. The study showed that the loading levels of urea phosphate in the composites were consistent and this method to develop controlled-release fertilizers can be used, not only in agriculture but also in other controlled-release applications.<sup>124</sup>

**6.1.2 Pesticide delivery.** By encapsulating pesticides within biodegradable polymers, the active ingredient is released only upon contact with specific targets like insect larvae or fungal spores. This reduces the amount of pesticide needed and minimizes harm to beneficial insects and pollinators. Liu *et al.* engineered three different carriers composed of PLA, namely microspheres, microcapsules, and porous microcapsules, by utilizing the premix membrane emulsification (PME) technique to regulate the release of Lambda-Cyhalothrin (LC). Out of these options, the microcapsule delivery method demonstrated better water dispersion in comparison to the other technologies. Due to their hollow form, the microcapsules exhibited significant buoyancy in water, which effectively hindered their settling. Conversely, microspheres with a solid core exhibited a high density, leading to fast precipitation. If the microcapsules are porous, water can enter the cores through the open pores, which leads to a loss of buoyancy and faster precipitation. Remarkably, the microcapsule devices exhibited a much-extended release of LC over a more extended period compared to commercial goods. The controlled release of LC may be precisely managed by manipulating the LC concentration and particle sizes of the microcapsules, which is influenced by both LC diffusion and matrix degradation.<sup>112</sup> In a separate investigation, scientists enclosed methomyl, a hydrophilic insecticide, into nano-capsules made from shell cross-linked structures. These structures were created by the self-assembly of photo-crosslinkable carboxymethyl chitosan (Az-CMCS) and were then exposed to intense UV irradiation. The nanocapsules demonstrated a high level of efficacy in encapsulating substances in a slightly acidic environment with a pH of 4.0. This is mainly due to the formation of hydrogen bonds between the methomyl molecules and the inner surface of the capsule. Diffusion was determined to be the driving force behind the release of methomyl from the different samples into an aqueous medium with a pH of 6.0. The researchers noted that the pace at which the substance diffused or was released was determined by the degree of cross-linking in the shell and its density of cross-linking. Furthermore, laboratory experiments on insecticidal activity against armyworm larvae revealed that the methomyl-loaded nanocapsules exhibit a much superior insecticidal activity compared to the original formulation.<sup>125</sup>

**6.1.3 Herbicide delivery.** Particles containing herbicides can be designed to target specific weeds based on their size, shape, or surface properties. This precise delivery minimizes collateral damage to desired plants and reduces herbicides' contamination in soil. Yu *et al.* engineered glutathione (GSH)-responsive nanoparticles derived from carboxymethyl chitosan (CMCS) and cross-linked them with disulfide bonds to achieve controlled herbicide release.<sup>126</sup> These nanoparticles were synthesized by assembling an amphiphilic derivative of carboxymethyl chitosan (CMCS-MUA) in an aqueous medium, followed by ultrasonic treatment to form disulfide cross-linking



bonds. Diuron was utilized as a model herbicide. *In vitro* release studies revealed that the release rate of diuron was significantly influenced by GSH concentration; specifically, a higher GSH concentration (2 mM) prompted a steady and sustained release of diuron. Additionally, increasing the substitution of hydrophobic MUA resulted in a slower release of diuron over time. Efficacy trials on *Echinochloa crusgalli* demonstrated the effectiveness of diuron-loaded nanoparticles in pre-emergence treatment.<sup>126</sup> In a similar quest, lab experiments were conducted to evaluate the effectiveness of herbicide formulations for controlling weed growth in wheat and barley plots. Various experiments were conducted with grain crops infested with individual weeds *A. retroflexus* and *A. fatua* L. or a combination of weeds *A. retroflexus* and *S. arvensis*, which demonstrated the superior efficacy of encapsulated metribuzin (MET) and tribenuron methyl (TBM) as compared to these herbicides in their free form (Fig. 13).

The formulations of poly-3-hydroxybutyrate (PHB) encapsulated with two herbicides, metribuzin (MET) and tribenuron-methyl (TBM), presented as films and microgranules, were tested against weed species with "wheat" (*T. aestivum*) as the main crop. Both the film and microgranules exhibited substantial efficacy in controlling weed infestation when compared to market formulations. The study concluded that degradable PHB could be a promising material for making slow-release herbicide formulations for pre-emergence weed treatment. Additionally, wheat treated with the experimental formulations exhibited notably higher biomass as compared to commercial formulations.<sup>127</sup>

Pereira *et al.* have demonstrated that the encapsulating atrazine (herbicides) proved to be efficient, resulting in stable formulations with modified release profiles governed by anomalous transport. The encapsulated herbicides showed enhanced efficacy against target organisms without harming non-target ones, suggesting improved bioavailability. Additionally, they increased atrazine's mobility in soil, enhancing effectiveness against target organisms while being less genotoxic as compared to the free herbicide.<sup>128</sup>

## 6.2 Soil improvement and crop protection

Beyond the controlled release of agrochemicals, biodegradable polymeric particles offer additional benefits for soil health and crop protection.

### 6.2.1 Soil stabilization and moisture retention. Particles

can be formulated to form a protective layer on the surface of soil, reducing wind and water erosion. Additionally, some polymers can absorb and retain moisture, improving water availability for plants during dry periods. Xiang *et al.* showed that superabsorbent polymers (SAPs) comprising polyacrylic acid and wheat straw (cellulose) based particles can better mitigate the inhibitory effects of heavy metals (HMs) present in the soil on the biodegradation and nutrient release of biodegradable polymers in contaminated soil.<sup>63</sup>

For instance, Kathi *et al.* evaluated the efficacy of corn starch-based SAP (super-absorbent polymer) particles in decreasing leachate and enhancing water accessibility for plants. Findings indicated that SAP particles derived from cornstarch augmented the soil's water-holding capacity, retaining more water, which helped to preserve nitrogen in the soil. Consequently, this led to increased water and nitrate availability for tomato plants, surpassing treatments with soil alone or soil with fertilizer only. Furthermore, the water and nutrient retention rates, which vary from 35% to 91% depending on the application rate of SAPs, show significant potential for conserving water and nutrients.<sup>70</sup>

### 6.2.2 Enhanced plant growth and stress tolerance. Parti-

cles loaded with beneficial microorganisms or biostimulants like seaweed extracts (SWEs) can promote plant growth, improve root development, and enhance stress tolerance against drought, salinity, or extreme temperatures. Applying SWEs to the foliage had a beneficial effect on the growth, yield, and quality characteristics of four onion varieties. Overall, the lowest concentration tested, 0.5% SWE, significantly influenced the nutrient content, yield, and total soluble solids of the onion varieties.<sup>100</sup> In another investigation, it was shown that treatments with seaweed extract notably increased the yield of wine

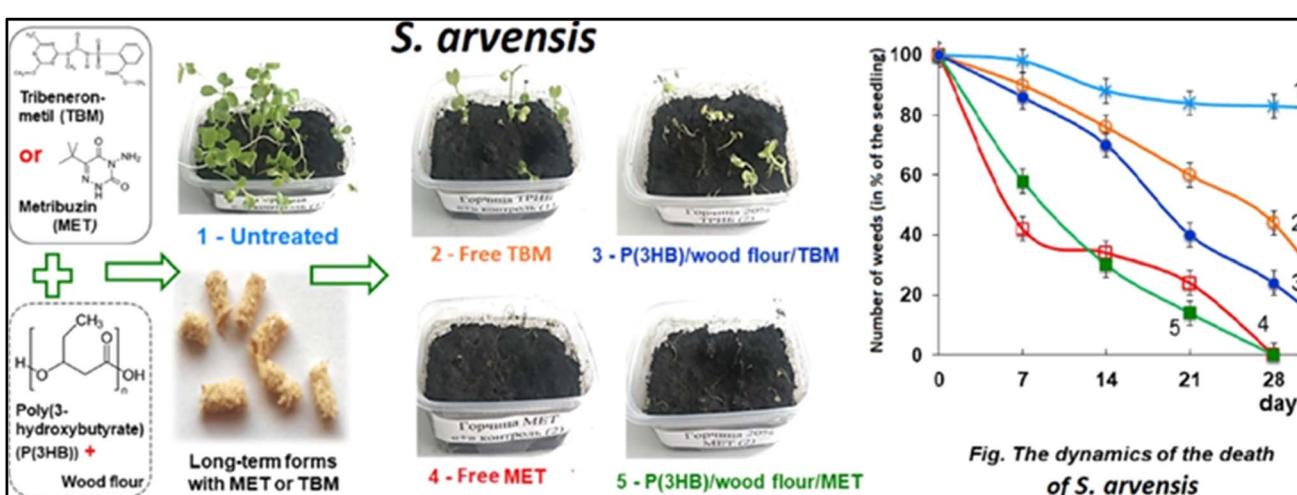


Fig. 13 Studying the effect of metribuzin and tribenuron methyl on controlling weed growth.<sup>127</sup>

grapes by 14.7%.<sup>129</sup> The encapsulated fertilizer, both micro- and macroalgal, provides vital growth nutrients and hormones to the plant. Additionally, it aids in managing diseases caused by pests and pathogens. Compared to the control group, the treated sample (seed encapsulated with algae) exhibited enhanced growth parameters.<sup>130</sup> The seaweed was encapsulated in chitosan solution at various concentrations (w/v%) ranging from 5% to 20%, utilizing sodium tripolyphosphate as a cross-linker, with the aim of investigating its potential application in fertilizer bead production.<sup>71</sup> Apart from fertilizers, other ingredients can also be encapsulated. Campos *et al.* encapsulated *Enterobacter* sp. (nitrogen fixing bacteria) with more than a 78% survival rate by using a spray-drying method. The matrix comprised sodium alginate and maltodextrin (1 : 14). This encapsulation protected the bacteria during the spray drying process and aided the activation of bacteria upon addition in the soil.<sup>108</sup>

**6.2.3 Targeted biocontrol delivery to provide disease resistance.** Biodegradable particles can be used to deliver biocontrol agents like beneficial bacteria and fungi directly to the plants' root zone. These agents help to suppress plant pathogens and improve overall plant health. Peli *et al.* developed a spore-compatible method called layer-by-layer assembly to encapsulate spores of a new mycoparasitic strain called *T. reesei* IBWF 034-05 within a lignin shell. This encapsulation prevents undesired premature germination, allowing for application as an aqueous dispersion *via* trunk injection. Initially, upon injection into a plant, the spores remain dormant. Subsequently, when lignin-degrading fungi infect the plant, the shell undergoes enzymatic degradation, selectively triggering germination by the pathogenic fungi, as demonstrated in laboratory tests. The germinated *Trichoderma* then counteracts the fungal pathogens, ultimately displacing them from the plant.<sup>131</sup> Beckers *et al.* fabricated fungicide-loaded nanocarriers of xylan, derived from corncobs *via* interfacial polyaddition using toluene diisocyanate (TDI) as a crosslinking agent. The aqueous dispersions of these nanocarriers exhibited *in vitro* efficacy against various pathogenic fungi. Additionally, the unfilled xylan-based nanocarriers stimulated the growth of fungal mycelium, which indicated degradation of xylan in the presence of fungi acting as a trigger for releasing loaded agrochemicals.<sup>132</sup>

By facilitating the targeted delivery of essential nutrients, bioactive compounds, and beneficial microbes, biodegradable polymeric particles hold immense potential for enhancing crop yield and quality. Improved nutrient efficiency, increased plant growth, and enhanced stress tolerance can lead to higher yields with optimal quality parameters.<sup>63,129,133–135</sup> Additionally, the targeted delivery of pesticides and herbicides minimizes damage to beneficial organisms, promoting a healthier agricultural ecosystem.<sup>58,112,136–138</sup>

### 6.3 Critical analysis of application areas

The application of BPPs in agriculture has progressed unevenly across different domains, namely controlled agrochemical release, soil improvement, plant growth and stress tolerance.

Below, we critically analyze the state of the art in these areas, highlighting their advancements, delays, and recommendations for future development.

**6.3.1 Controlled agrochemical release.** Controlled-release systems for fertilizers and pesticides are the most advanced applications of BPPs. These systems have been extensively studied and field-tested, with several formulations showing commercial potential. For instance, encapsulated fertilizers have demonstrated the ability to improve nutrients' use efficiency by minimizing leaching and ensuring prolonged nutrient availability. Similarly, pesticide-loaded particles have shown enhanced target specificity and reduced environmental impact. The maturity of this application is due to established manufacturing techniques, such as spray drying and solvent evaporation, which allow precise control over particle size and release profiles.<sup>45,57,139</sup> A high market demand for technologies that improve agricultural productivity, while reducing chemical runoff, further promotes their widespread adoption.<sup>54,140</sup>

Despite these advancements, cost and scalability still remain as challenges. The use of biodegradable polymers, such as polylactic acid (PLA), increases production costs, and achieving consistent particle quality on an industrial scale is an unmet need.<sup>141,142</sup>

Nevertheless, Controlled-Release Fertilizers (CRFs), such as controlled-release urea (CRU), have demonstrated significant improvements in nitrogen's use efficiency (NUE) and grain yield as compared to conventional urea. For example, incorporating CRU at 300 kg N ha<sup>-1</sup> increased NUE by 27.6% and 22.9% in rice as compared to conventional urea over two consecutive years. Additionally, CRU applied at 200 kg N ha<sup>-1</sup> (*i.e.*, one-third less nitrogen) produced 3–5.9% higher grain yield than conventional urea applied at 300 kg N ha<sup>-1</sup>, highlighting CRU's efficiency in meeting the crop nitrogen demand while reducing fertilizer use.<sup>5</sup>

Field studies in wheat and maize crops have shown that blended CRU formulations increased wheat yields by 7.9–10.3% and maize yields by 9.1–21.0% as compared to normal urea at equivalent application rates. The NUE was enhanced by 33.7–56.4% for wheat and 16.7–48.5% for maize, and the average annual net profit rose by 14.5–19.9%. These results indicate that CRU fulfills the crop nitrogen demand throughout the growth period, minimizes nitrogen losses, and reduces the need for multiple fertilizer applications, lowering both labor and environmental costs.<sup>143</sup>

Interestingly, CRU closely matched the nitrogen requirements of rice, thus enhancing the root zone's N concentration and leaf enzyme activity (GS, GOGAT, and NR), resulting in reduced fertilizer use and higher yields.<sup>144</sup> CRU's environmental benefits are profound. Studies show that blending CRU with conventional urea in bulk blending urea (BBU) systems decreased reactive nitrogen (Nr) losses by 35.6–54.5% and reduced greenhouse gas (GHG) emissions by 34.1–44.7%. Moreover, N and C footprints were lowered by 41.1–60.8% and 41.8–42.3%, respectively, significantly mitigating ecological impacts. These outcomes clearly demonstrate that CRU-based systems effectively balance productivity and sustainability in agricultural practices.<sup>5</sup>



**6.3.2 Soil improvement.** Applications of BPPs in soil improvement are less developed as compared to those of controlled-release systems. These include superabsorbent polymers for moisture retention and soil stabilization particles. Laboratory studies have demonstrated their ability to enhance soil health and water-use efficiency, particularly in arid regions.<sup>17,63,145,146</sup> However, the adoption of these technologies is limited by the lack of extensive field trials across diverse soil types and climatic conditions.<sup>121</sup> Uncertainty about the long-term impact of polymer degradation products on soil microbial communities and overall soil fertility impedes their widespread adoption.<sup>147–151</sup>

To bridge this gap, research should focus on field validation of these technologies and evaluating the ecological compatibility of biodegradable polymeric residues.

**6.3.3 Plant growth and stress tolerance.** The use of BPPs to deliver biostimulants or beneficial microbes for plant growth and stress tolerance is still in its infancy. These particles show potential for targeted delivery of drought-resistance agents and growth-enhancing nutrients.<sup>57,88,101,152</sup> However, this application is delayed due to the sensitivity of encapsulated bioagents, which complicates manufacturing and storage.<sup>73,86,153,154</sup> The limited scalability of encapsulation techniques like ionotropic gelation and electrospinning<sup>72,102,106</sup> and sparse field data on the efficacy of these systems in diverse agricultural settings<sup>5,143</sup> also contribute to the challenges in their applications.

Advancing this area will require interdisciplinary research to optimize the compatibility of biodegradable particles with plants and soils, as well as the development of cost-effective production methods for scaling up.

Controlled agrochemical release systems should focus on reducing production costs and optimizing scalability to achieve wider adoption. Soil improvement technologies need thorough field testing and ecological impact assessments. Plant growth and stress tolerance applications require scalable encapsulation techniques and comprehensive field validation. The challenges identified—high costs, scalability issues, and regulatory hurdles—are further explored in the next section, where potential solutions to advance these technologies are discussed.

## 7. Challenges

Despite their immense potential, biodegradable polymeric particles face some significant challenges that need to be addressed prior to their widespread adoption in agricultural fields.

- **Cost-effectiveness.** Currently, the production cost of biodegradable polymeric particles containing actives is significantly higher as compared to conventional fertilizers and pesticides. This can be a barrier for small-scale farmers and limit their widespread applicability. Research efforts focusing on cost-reduction strategies through material selection, production techniques, and large-scale manufacturing are crucial.

- **Delivery system optimization.** Fine-tuning the delivery system of biodegradable polymeric particles is essential for maximizing their effectiveness. This involves optimizing the

particle size, surface properties, and release profiles for specific applications. For instance, particle size needs to be tailored for efficient uptake by plants or soil microbes, while release profiles should match the specific nutrient's requirements at different stages of plant growth. Sometimes, it is difficult to achieve multiple requisites from a single particular system.

- **Long-term impact assessment.** While biodegradable polymeric particles are designed to decompose naturally, to understand the long-term effects of their degradation products on soil health, detailed investigations are required. Prior to their application, the materials' toxicity and their interactions with biological entities should be evaluated using various techniques such as SAR (structure activity relationship), molecular modelling, predictions based on available data reported in the literature, *etc.* A thorough evaluation of potential impacts of the released actives as well as the employed polymers on soil microbial communities and overall soil fertility is necessary for ensuring the long-term sustainability of this technology.

## 8. Future directions

The field of biodegradable polymeric particles in agriculture is an emerging and rapidly evolving area. Current research is moving beyond single-purpose particles towards the development of multifunctional particles that can address multiple agricultural needs simultaneously. Imagine particles that encapsulate both essential nutrients and pesticides and simultaneously deliver a controlled dose of pest control agents and nutrients at a desired location. Multifunctional particles streamline application processes, reducing the need for multiple treatments and saving time and resources for farmers, in addition to improving the overall health and economy. Combining functionalities within a single particle can lead to synergistic effects. Some nutrients can enhance the efficacy of certain pesticides, leading to improved pest control with lower doses, thereby providing environmental and economic benefits. The development of multi-functional particles offers another frontier for exploration. For instance, encapsulating multiple agrochemicals within a single particulate system may further enhance agricultural efficiency and sustainability. For example, combining a pre-emergent herbicide with a nitrogen fertilizer in one polymer matrix controls weeds while supplying essential nutrients to the desired plant, reducing the need for multiple doses of various actives. These particles may simultaneously deliver nutrients, control pests/unwanted herbs and improve soil health, thus providing comprehensive solutions for sustainable farming practices. Moreover, by minimizing the number of requisite doses, multifunctional particles can further reduce the environmental footprint of agricultural practices, thereby enhancing agricultural sustainability. Dual delivery of insecticides and fungicides in nanocapsules can protect crops like tomatoes from pests and diseases simultaneously. Similarly, a nematicide combined with beneficial microbes in a single carrier may improve root health, while controlling nematodes. In this regard, few studies have already been conducted that showed that dual loading of pesticides in a single



polymeric carrier can provide synergistic effects and be more efficient than commercially available formulations.<sup>160,161</sup> For instance, Dhiman *et al.* prepared dextrin-based microgels for slow release of dual fertilizers.<sup>162</sup> Other combinations may include pesticides with plant growth regulators, herbicides with soil conditioners and fungicides with bio-stimulants; all may be tailored to enhance the crop health and productivity, while minimizing environmental impact.

One more key area for advancement lies in the development of smart and stimuli-responsive particles that release agrochemicals in response to specific environmental triggers such as soil pH, moisture, or temperature. These systems can ensure precise delivery and minimize wastage as well as environmental contamination. Additionally, the potential for biodegradable polymeric particles in biofortification remains largely untapped. By delivering essential micronutrients such as zinc and iron directly to crops, these systems can enhance nutritional quality while maintaining environmental balance. Moreover, most of the degraded fragments of biodegradable polymers may act as nutrients for growing plants, thus further enhancing the soil health and contributing positively to the environment.

To accelerate adoption, large-scale field trials and long-term impact assessments are essential. Such studies would validate the ecological and agronomic benefits of these particles under diverse agricultural conditions. Finally, advancing cost-effective and sustainable fabrication methods such as using agricultural waste as raw materials will make these technologies more sustainable and accessible to small-scale and resource-constrained farmers, driving widespread adoption. By addressing these areas, future research can unlock the full potential of biodegradable polymeric particles, transforming them into essential tools for sustainable and resilient agriculture.

## 9. Conclusions

Applications of biodegradable polymeric particles in agriculture present a transformative approach to addressing some of the most pressing environmental and sustainable challenges faced by traditional farming. This review highlights the significant potential and versatility of biodegradable particles in providing controlled release of fertilizers, pesticides, and herbicides, as well as their role in soil remediation and plant growth enhancement. Biodegradable polymers offer an eco-friendly alternative to conventional plastics, mitigating the adverse impacts associated with plastic pollution. Their ability to decompose naturally in the soil environment through abiotic and biotic processes ensures minimal accumulation and toxicity, thereby promoting soil health and reducing environmental contamination.

While the advancements in active containing polymeric particle fabrication techniques, such as emulsion-based methods, spray drying, coacervation, and nanoprecipitation, have enabled the precise control of particle size, loading efficiency, and release kinetics, challenges remain. These include the high cost and scalability of the production, potential long-

term environmental impact of degraded products, regulatory hurdles, and the need for performance optimization. Nevertheless, the future of biodegradable polymeric particles in agriculture still holds immense potential for innovation and impactful applications.

This review highlights the transformative potential of BPPs in advancing sustainable agriculture. By focusing on key applications such as controlled agrochemical release, soil improvement, and plant stress tolerance, it provides a targeted analysis of their utility and addresses the barriers to their adoption, including cost, scalability, and regulatory challenges. Unlike prior studies, this review aligns its discussion closely with agricultural applications, offering a practical framework for researchers and practitioners to develop field-ready solutions. Addressing the identified gaps will not only drive innovation but also contribute to achieving global agricultural sustainability goals.

Ultimately, future research should focus on developing cost-effective and scalable production methods, after thoroughly evaluating the environmental safety of degradation products, and optimizing the performance of active loaded biodegradable polymeric particles. Collaboration between scientists, industry stakeholders, and regulatory bodies will be crucial in establishing clear guidelines and standards to facilitate the adoption of these materials in agricultural practices. In conclusion, biodegradable polymeric particles hold great promise for enhancing agricultural productivity, sustainability, and environmental protection. Continued innovation and research in this field are essential to fully harness their potential and pave the way for a more sustainable and resilient agricultural future.

## Data availability

This review article is based on previously published research and does not involve the generation of new datasets. All data supporting the findings and discussions presented are available within the cited references. No new data were created or analyzed in this study. Further information regarding specific studies referenced can be obtained from the corresponding publications.

## Conflicts of interest

There are no conflicts to declare.

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