MINI-REVIEWS



Polymeric nanoparticles as effective delivery systems in agriculture sustainability

Madhavi Vemula¹ · A. Vijaya Bhaskar Reddy²

Received: 24 June 2022 / Accepted: 13 March 2023 / Published online: 13 April 2023 © The Author(s), under exclusive licence to Springer Nature Switzerland AG 2023

Abstract

There is a continuous demand on the agricultural sector to enhance the crop production in order to fulfil the food requirements of increasing global population. Favourably, nanotechnology has provided innovative and significant advantages in agricultural sector by augmenting the crop yields and by protecting crops against pathogens. On the other hand, the advanced polymeric nanocomposites have proved to be the smart delivery systems for agrochemicals including fertilizers, insecticides, pesticides and other plant growth regulators owing to their higher stability, solubility, uniform distribution and controlled release. Besides, the recent research has also confirmed that the utilization of polymeric nanoparticles as delivery systems enhanced the efficiency of agricultural inputs by delivering agrochemicals more effectively and subsequently lead to agriculture development. In light of this, the current review summarizes the advanced synthesis methods of various nature-derived polymeric nanoparticles and their application towards the improved targeting, controlled release and lower losses of agrochemicals, by which high efficiency/crop yields and lower environmental impacts can be achieved compared to traditional formulations of agrochemicals. The review ends with a perspective on the fate of polymeric nanoparticles followed by concluding remarks on future directions of polymer nanoparticles in sustainable agriculture.

Keywords Polymer nanoparticles · Modern agriculture · Plant growth · Agrochemicals · Food science

Introduction

The prime focus of sustainable agriculture is to produce long-term crops and livestock to meet the society's food and textile requirements for the surging global population without compromising the ability of future generations to meet their own needs. Furthermore, sustainable agriculture tries to establish a good balance between the production of sustainable food production and the preservation of ecological system within the environment. The current agricultural practices are striving towards the sustainability due to the exploitation of natural resources by the extensive use of agrochemicals and their impact on environment. In response

Madhavi Vemula madhuchem9@gmail.com

A. Vijaya Bhaskar Reddy vijay.dr555@gmail.com

to the environmental impacts such as soil degradation, climate change, water pollution and emerging pathogens and disease causing agents, the research and development has been striving for new employable and safer technologies [6, 12, 50, 53]. Sustainability in agriculture has always been a primary concern providing a framework for the selection of the best combination of approaches in agricultural productivity [19].

The introduction of nanotechnology in agricultural sector has provided several potential benefits including the reduction in agricultural inputs, enhancement of food quality and safety, and enrichment of absorbing nanoscale nutrients from the soil. Undoubtedly, the sustainable growth of agriculture largely depends on innovative techniques like nanotechnology [53]. The significant interests of using nanotechnology in agriculture includes specific applications like nanofertilizers and nanopesticides to trail products and nutrients levels to increase the productivity without decontamination of soils, waters, and protection against several insect pest and microbial diseases [28]. In modern agriculture, sustainable production and efficiency are unimaginable without the use of agrochemicals such as pesticides and fertilizers. However,

¹ Department of Chemistry, BVRIT HYDERABAD College of Engineering for Women, Hyderabad 500090, India

² Department of Chemistry, Atria Institute of Technology, Bengaluru 560024, India

these agrochemicals pose considerable threats to human beings and ecosystem when contaminated with soil and water bodies. Therefore, effective technologies that reduce and/or eliminate the influence of modern agriculture on the environment and enhance the crop yields are highly desirable [52]. The emergence of scientific capabilities across the globe have unfolded the viable and promising techniques to contend these issues.

In recent years, polymer-based nanoparticles have been appeared as safe option for the delivery of agrochemicals without polluting the soil and air. The polymer nanoparticles protect the active ingredients of agrochemicals by minimizing interactions of the encapsulates with the environment through a coating. These approaches also relate controlled release of agrochemicals [70]. Also, the outlook is gradually shifting towards the use of natural polymers such as polysaccharides [36]. The significant advantage of natural polymers is that they are degradable by soil microorganisms and results environmentally non-toxic products when compared to their non-degradable synthetic counterparts [34]. Furthermore, the combined use of nanoparticles and polymers in encapsulation agrochemicals improves the sustainability and provides new research opportunities for the evaluation of their efficiency compared to the conventional formulations [16]. Polymeric nanocarriers can also act as more sustainable alternatives to other conventional materials with respect to the biocompatibility and material integrity thereby keeping down the potential of ecotoxicity [56]. This review intends to serve as a fundamental for agricultural researchers to instigate on the development and application of polymeric nanoparticles (PNPs) as nanocarriers in delivery systems for the agricultural sustainability. Further, the significance of nanoformulations in encapsulation and controlled release of agrochemicals has been discussed comprehensively. Next, the various synthesis methods of PNPs through dispersion and polymerization approaches have been presented in detail. Subsequently, the encapsulation of agrochemicals into PNPs followed by the fate of PNPs on environment is described extensively followed by the future implications of PNPs.

Emergence of polymeric nanoparticles

In general, agrochemicals are used to improve the crop yield and productivity, decrease crop losses, combat plant diseases and to improve food quality [10]. However, agrochemicals are hazardous and pose threat to the ecosystem after their leaching, degradation, volatilization and photolysis. In this context, nanotechnology has emerged as a choice of technology to overcome the above listed disadvantages and provided effective results for the controlled release of agrochemicals and subsequently improved crop yields. The essence of "nano" in science and technology has provided unique properties to the materials having the size range between 1 and 100 nm, which are highly desirable for practical applications. Nanoparticles and nanobased composites are very useful to enhance the controlled release of agrochemicals including pesticides, fungicides, herbicides and fertilizers protecting bioactive compounds from premature degradation [48, 57, 59].

Polymer nanoparticles (PNPs) are simplest soft materials and are proved to be capable to serve as sustainable alternatives in various branches of technologies over the years [1]. The PNPs can be synthesised through various routes including size downscaling, new phase transition and are explored into different approaches like self-assembled nanostructures, nonself-assembled nanostructures and number of nanoscale dimensions. The decreased size of polymer nanoparticles without changing their molecular arrangement from bulk size imparts various quantum impacts that lead to many folds increase in surface to volume ratio prevailing unique and exceptional properties [18]. This advancement has created great interest in community to develop PNPs for their applications in various domains including environment, medicine, science and technology. The PNPs with excellent physicochemical properties are significant in the development of various bionanomaterials and offer sustainable solutions in the field of agriculture to enhance the productivity and protection of crops [60, 61].

Owing to their biodegradability, biocompatibility, costeffectiveness, augmented productivity and lower toxicity, PNPs have received significant consideration for various agricultural applications [30]. It is believed that PNPs could overcome the disadvantages of conventional methods with better results at lower doses and are expected to lower the risk of environmental toxicity. Considering the environmental aspects, PNPs can precisely encapsulate agrochemicals and enhance their aqueous dispersibility and bioavailability thereby extends the effective lifetime of active ingredients. PNPs by encapsulating the active ingredient either by physically or chemically binding within the core of nanoparticles, release the agrochemicals in predetermined way by the cleavage of chemical bond or by physical diffusion [7].

These PNPs can be fabricated using various types of biodegradable, synthetic or natural polymers. Most popularly, chitosan, pectin, carboxymethyl cellulose have emerged as promising and favourable natural polymers for the controlled delivery of agrochemicals with improved stability [8]. Among the synthetic polymers, polyethylene glycol (PEG), polyvinyl alcohol (PVA), polylactide-co-glycolides (PLGA), polyepsilon caprolactone (PCL), polycitric acid(PCA) are used for nanoagroparticle formulations [67, 68]. Polymeric nanoparticles with perspective ratio of ingredients have been found satisfactory and present excellent substitutes for their enlarged potential applications in modern technologies [5, 45].

PNPs can be fabricated either from pre-existing polymers or by the direct polymerization of monomers [32]. Based on various requirements of PNPs such as release pattern, solubility and desirable penetration of agrochemicals, welldesigned nanostructured delivery systems with size and charge control, surface, physical and chemical properties are necessary. The choice of polymers to employ in agricultural applications should possess selective properties like stability, permeability, transmission on which the growth and protection of crops depends significantly [4]. In this perspective, functionalization of polymers or PNPs with improved characteristics have become an overwhelming domain and gained the attention of scientists globally.

Nanoformulations in encapsulation of agrochemicals and controlled release

Encapsulation is a technique intended to surround the active ingredient in the core maintaining the chemical stability [66]. The active ingredient from the encapsulated system releases into the environment under certain conditions for a predetermined time by breaking the core and dissolves after reaching the target. Encapsulation technique also generates a new product with improved storage and transportation properties, better synthesising formulation and greater particle size. The performance of encapsulated PNPs depends on the technology, formulation of the shell material, physicochemical properties of the active ingredient and release mechanism [17]. The active part of agrochemicals in the formulation gets protected from the external forces such as light, water, pH, temperature, oxidation and evaporation. Based on the particle size of coating material, there are two types of encapsulation techniques, i.e. microencapsulation and nanoencapsulation [64]. Microencapsulation deals with the change of colloidal and surface properties of a shell material that encapsulates the active ingredient with a diameter size of 1–1000 µm [62]. Common release profiles in this technique are zero-order, immediate (burst) and retarded release.

Nanoencapsulation is a promising technology with the particle size ranges in nanoscale in which the active ingredients are effectively released in slow, controlled and gradual manner from the particles. The release mechanisms such as diffusion, dissolution could play major role in the delivery of nanoencapsulated materials [2].

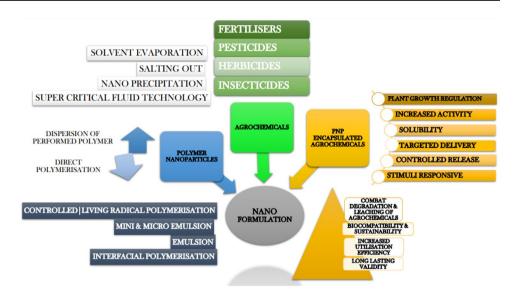
Table 1 shows the major differences between micro- and nanoencapsulation. The possible advantages of nanoencapsulation compared to microencapsulation includes the increased biological activity or performance, faster dissolution, better distribution and soil mobility [44]. Nanostructured systems owing to their unique properties can be used as carriers of agrochemicals (active ingredient) to combat loss of efficiency and increased productivity. PNPs are innovative materials reported for the controlled release of agrochemicals and their targeted delivery. PNP formulations are prepared to encapsulate the active ingredient of agrochemicals using different techniques. The main purpose of the encapsulation of agrochemicals by smart delivery systems utilise PNPs enabling the accurate and targeted delivery with the goal of obtaining larger yields over a longer period of time. The technical advances in PNP formulations discriminate the abusive use of agrochemicals with extended benefits of stimuli response, reduced dosing frequency and prolonging activity. Biodegradable polymers used in nanocarrier systems such as chitosan, carboxymethyl cellulose, alginic acids, polylactic acids, polyglycolic acids, polycaprolactone are considered as promising in advancing agricultural technologies that are safe and efficient [20].

The main functions of polymer nanoscale carriers are to retain the agrochemicals until it reaches the target, to enhance the aqueous dispersibility and bioavailability until it reaches the target and extends the lifetime by controlling the active release functions in neighbouring environment [21]. The release pattern of active ingredient from the polymer matrix is generally illustrated in terms of diffusion, swelling or relaxation and surface or bulk erosion of nanoparticle [22]. Figure 1 shows the nanoformulations of polymers with various types of agrochemicals that can be encapsulated, methods to prepare polymer nanoparticles, properties and strategies of advantages of PNPs in agriculture.

Table 1 Differences between microencapsulation and nanoencapsulation [17]

Microencapsulation	Nanoencapsulation	
Dependent on technology, material chemistry and composition	Less influenced on technology and more by materials	
Capsule dispersions and powders are usually obtained	Nanoparticle powders are more difficult to achieve	
Smaller surface to volume ratio	Larger surface to volume ratio	
Larger shell thickness	Smaller shell thickness	
Comparably less performance	Comparably increased biological activity or performance and soil mobility	
Exhibit less dispersibility, stability and dissolution	Easily dispersible, exhibit high stability and faster dissolution	

Fig. 1 Nanoformulation of polymers with various agrochemicals, properties and advantages of PNPs in agriculture



These release pattern functions depend on size, shape and synthesizing formulations, i.e. combinations of different materials used for synthesis of nanocarrier [46]. The other factors like solubility, density, crystallinity, orientation, polarity, chemical degradation, cross-linkage and biodegradability affects the release of agrochemicals. In addition, temperature, pH, humidity, pressure are also the external parameters that result in controlled release. Encapsulation by PNPs allows protection of agrochemicals from external forces like light, water, oxidation and evaporation for the improved storage [11].

Synthesis of polymer nanoparticles

PNPs have been conveniently prepared by dispersing the preformed polymers (top-down approach) and the direct polymerization of monomers (bottom-up approach). Methods like desolvation, dialysis, salting-out, solvent evaporation, nanoprecipitation, spray drying, and supercritical fluid technology have been employed for the preparation of PNPs from preformed polymers [26, 55]. PNPs can also be synthesized by direct polymerization of monomers using several techniques such as emulsion, mini- and micro-emulsion, interfacial and controlled/living radical polymerization. The method chosen to synthesize PNPs depends on the nature of polymeric system, area of application, surfactant, active component and other additives.

Dispersion of preformed polymers

Due to the versatility of PNPs, several methods have been reported for the preparation of PNPs and utilized successfully by dispersing the preformed polymers.

Solvent evaporation

Solvent evaporation is very common technique that emerged to prepare PNPs from a preformed polymer [69]. Briefly, the polymer is dissolved in an organic phase into which active ingredient is included by dissolution/dispersion. The resulting solution is added to aqueous phase that contains surfactant/emulsifying agent and is processed by using ultrasonication or homogenization to form an emulsion [3]. The solvent is evaporated on formation of stable emulsion either by continuous stirring or by increasing the temperature at reduced pressure. The nanosuspension is then washed and freeze dried to acquire fine powder of nanoparticles.

Salting-out

Salting-out process is formulated without employing any surfactants/emulsifying agents and chlorinated solvents. This method involves dissolution of polymer in the organic phase, which is totally miscible with water, like acetone, tetrahydrofuran and emulsified under strong shear stress [15]. The aqueous phase contains high concentration of salt that are insoluble in organic phase. In general, magnesium chloride, calcium chloride and magnesium acetate [43, 72] are used in 1:3 polymer to salt ratio. The addition of such salts modifies the miscibility properties of water

with other solvents. By the addition of large excess of water to the emulsion under gentle stirring decreases the ionic strength and leads to the precipitation inducing nanosphere formation. Finally, centrifugation is used to remove the salting-out agent from the nanoparticles.

Nanoprecipitation method

The nanoprecipitation method was formulated for the synthesis of PNPs [14]. This method results in instantaneous formation of nanoparticles can be scaled up easily and is a one-step procedure. The process is based on the interfacial deposition of a polymer after displacement of a semipolar solvent that is water miscible. PNPs are formed instantaneously by adding the organic phase slowly to the aqueous phase under gentle stirring by rapid diffusion. Although the surfactant is not required in this method, the nanosuspensions can be prevented from agglomeration by adding surfactants. Moreover, the nature and concentration of surfactant influence the size of nanoparticles [25].

Supercritical fluid technology

As the preceding methods involve organic solvents, supercritical fluid technology can be strategically less harmful to the environment for the potential production of PNPs with high purity [24]. Supercritical fluids have low and tuneable densities allowing them to have transition from gas to liquid with ease, through a small change in pressure at constant temperature. This method is interesting and expected to produce nanoparticles evading most of the limitations of traditional methods. Two principle processes have been emerged for the production of nanoparticles using supercritical fluids;

(a) Rapid expansion of supercritical solution (RESS)

In this process, the solute dissolves in a supercritical fluid and the solution rapidly expands into the ambient air through the capillary nozzle. The degree of supersaturation followed by rapid pressure reduction has considerable impact on the particle size, morphology and dispersity of the particles. The method produces microscaled rather than nanoscaled particles.

(b) Rapid expansion of supercritical solution into liquid solvent (RESOLV)

With this technique, the researchers have modified the RESS technique to expand the supercritical solution into a liquid solvent instead of ambient air. The RESOLV technique primarily reduces the coagulation rate in the free jet expansion of RESS. This technique produces nanosized particles as liquid solvent suppresses the particle growth in expansion jet making it feasible to overcome the limitations of RESS technology.

Polymerisation of monomers

Polymerisation of monomers fabricates PNPs with required properties for a particular application. Few techniques that produce PNPs through polymerisation such as mini-, microand emulsion polymerisation techniques that are progressed recently in use are discussed. In addition, other hetero-phase polymerisations such as interfacial and living/controlled radical polymerisation utilised in preparation of PNPs are conferred.

Emulsion polymerisation

Based on the use of surfactant, this approach can be categorized into conventional and surfactant-free polymerisation. In conventional emulsion polymerisation, colloidal stabilisers such as electrostatic, steric or electrosteric are used and the surfactant required to be removed from the final product. As the removal of surfactant is time consuming and increases the cost of production, surfactant-free emulsion polymerisation has been emerged significantly to prepare PNPs by emulsion polymerisation [31]. In this method, stabilization of PNPs can be obtained through the use of ionisable initiators or ionic co-monomers. Hence, surfactantfree emulsion polymerisation has manifested as a simple and green method for PNP production.

Miniemulsion

Miniemulsions are typical class of emulsions that are stabilised by a surfactant and are produced by high-energy homogenization and usually yield stable droplets [9]. Polymers, in this technique are usually synthesized in the dispersion phase at the interface of the droplets. A large range of polymers can be generated by miniemulsion due to their colloidal properties and stability. The functional polymers have been synthesized by researchers by miniemulsion method for their specific properties and their applications in various fields.

Micro-emulsion

Micro-emulsion polymerisation is an effective approach for synthesis of PNPs. Though micro-emulsion polymerisation generates colloidal polymer particles with high molar mass, similar to emulsion polymerisation, the kinetics of microemulsion is different comparatively. The polymerisation depends on high quantities of surfactant systems lowering the surface tension of materials, thereby completely covering the surface of particles. Micro-emulsion method produces considerably smaller number of chains per particle and particle size [23]. Interfacial polymerisation is one of the preparation strategies to fabricate PNPs [39]. This is a type of step-growth polymerisation occurs at the interfacial region of the two miscible liquid phases, endowing PNPs with unique topological and chemical properties. A number of varieties of PNPs such as ultra-thin films, nanocapsules, and nanofibres can be prepared using this method. Various types of interfacial polymerisation such as liquid–solid interfaces, liquid–liquid interfaces and liquid-in-liquid emulsion interfaces are approachable [63]. Several polymers, e.g. polypyrrole, polyaniline, polythiophene, etc., have been synthesized by interfacial polymerisation.

Controlled/living radical polymerisation

Free radical polymerisation, one of the most widely employed approaches for polymerisation, has some constraints such as poor control of molecular weight and its distribution. The recent emergence of controlled/living radical polymerisation is one of the most useful techniques for the development of PNPs with desired molecular size, design and size distribution. These polymerisations stop only when there is no monomer and not when termination occurs. The concentration and nature of monomer, control agent, initiator and emulsion type are considerable imperative parameters in determination of the PNP size. The PNPs with narrow molecular weight distribution can be achieved by various strategies like atom transfer radical polymerisation, reversible addition-fragmentation chain transfer polymerisation and nitroxide-mediated polymerisation [33, 42].

Polymer nanoparticles as carriers of agrochemicals

PNPs act as carrier systems for agrochemicals in agriculture that transport these substances in a slow and controlled approach, due to their high surface/volume ratio. Research showed that nanometric particle size is considered to have subsistence for the controlled delivery of agrochemicals as nanoparticles possess advantages such as easy fixation and accelerated mass transfer [58]. The chemical properties specifically in polymeric materials with nanometric scale may be attributed to present various advantages imperatively such as the better mode of action/interaction at the target site of plant due to their tuneable-controlled release properties conferring an artificial immune system in plants [13, 48]. These smart delivery systems confer more selectivity without restraining the agrochemicals activity with potential formulations towards the target. Additionally, the PNP formulation reduces the troubles associated with drifting and leaching and leads to a more effective interaction. These features associated with PNPs enable to use very smaller number of agrochemicals per area as the formulation provides an optimal concentration delivery for prolonged time. Hence, it is not required for further application of agrochemicals reducing the phytotoxicity and the environmental deterioration to other nontargeted organisms [35, 51]. Few examples of polymer nanocarriers that have been utilised for agrochemical delivery are outlined in Table 2. In one of the studies, Tong et al. demonstrated the block copolymer of biocompatible polyethylene glycol and biodegradable polylactic-coglycolic acid as a carrier of metolachlor herbicide. These PNPs were shown to have good water solubility and lower toxicity towards nontarget human cells when compared to free herbicide [67, 68].

In another report by Maruyama et al. nanoencapsulation of herbicides such as imazapic and imazapyr in alginate-chitosan and chitosan-tripolyphosphate polymer nanoparticles was acquired by ionotropic gelation. When compared to the results

 Table 2
 Polymer nanocarriers used in Agrochemical delivery

Polymer used as Nanocarrier	Agrochemical Used	Nature of Carrier	Release Property	References
Chitosan-Alginate	Imazapic	Nanoparticle	Diffusion	Maruyama
Chitosan-Alginate	Imazapyr	Nanoparticle	Relaxation of polymer matrix	Maruyama
Poly(e-caprolactone)	Atrizine	Nanocapsule and Nanosphere	Diffusion and relaxation of Polymer matrix	Pereira
Polyacrylate	Emamectin benzoate	Nanoparticle	-	Shang
Chitosan-pectin	Carbendazim	Nanoparticle	Diffusion	Kumar
Nanocellulose	NPK fertilzer	Nanoparticle	Diffusion	Messa
DPPE conjugated chitosan-co-PLA	chlorpyrifos	Nanoparticle	Diffusion	Zhang
azidobenzaldehyde-functionalized chitosan	methomyl	Nanocapsule	pH responsive	Sun

of free chemicals, they discovered that these nanoencapsulated herbicides were more efficient and had lower genotoxicity. Pereira et al. reported the effects of nanocapsules and nanospheres of poly ((ϵ -caprolactone) for the substantial delivery of the atrazine, an herbicide in both target and nontarget plant species. It was found that nanocapsules have lesser physiological stability compared to nanospheres due to aggregation of nanocapsules. However, both nanospheres and nanocapsules were loaded at almost 90% encapsulation efficiency with prolonged release into water and exhibited less genotoxicity when compared to free atrazine. Shang et al. reported the enhanced pesticide photostability of polyacrylate nanoparticles bearing emamectin benzoate in the polymer framework. N-acrylate emamectin benzoate was copolymerised with butyl acrylate and methyl methacrylate by emulsion polymerisation. The experimental results demonstrated that the nanoformulation showed greater photostability compared to the commercial emamectin benzoate. Laboratory studies showed that nanoformulation demonstrated significant prevention and treatment effects against Helicorvapa armigera than the control.

Chitosan-pectin nanoparticles loaded with carbendazim, an active pesticide was prepared by Kumar et al. by ionic interaction method to impede Fusarium oxysporum and Aspergillus parasiticus. The nanoparticles with size 70 and 90 nm were obtained and exhibited 100% inhibition of fungi at 0.5 and 1.0 ppm concentrations, respectively. The carried-out laboratory tests concluded that nanoformulated carbendazim is noticeably more effective and protective for the germination and root growth of cucumber seeds than the pesticide applied directly. In another study, Sigmon et al. fabricated the biodegradable polymer nanocomposites containing polyhydroxyalkanoate (PHA) and calcium phosphate nanoparticles (Ca-P-NPs) and evaluated the delivery of a Phosphate nutrient, and assessed the efficiency. PHA-Ca-P polymer nanocomposites have showed sustained plant performance comparably to the control and found the significant reduction in nutrient loss from the soil over 80%.

Messa et al. reported the preparation and properties of the persistent release of NPK fertilizer based on nanocellulose. The inclusion of 10 wt% nanocellulose to microparticles resulted in the considerable reduction in fertilizer release rate within 5.0 h. Their work demonstrated the possible use of sulphated nanocellulose in biopolymeric framework to fabricate-enhanced fertilizer release systems. Zhang et al. synthesized an amphiphilic copolymer of chitosan with poly(lactide) and1,2-dipalmitoyl-sn-glycero-3-phosphoethanolamine (DPPE) by nanoprecipitation method and loaded with chlorpyrifos, an organophosphorus pesticide for control delivery. Utilization of this nanoparticle system has prolonged the pesticide release time and showed enhanced stability due to the amphiphilic nature of the copolymer.

Encapsulation of hydrophilic Methomyl pesticide in crosslinked nanocapsules of copolymer of azido benzaldehyde and carboxyl methyl chitosan was reported by Sun et al. The result showed that the encapsulation efficiency was maximised to 90% in aqueous medium at pH 4.0. Release profile of methomyl loaded nanocapsules was shown to be diffusion controlled and the insecticidal activity was significantly superior to the non-nanoformulated methomyl compound.

Fate of polymer nanoparticles

Polymer nanoparticles own distinct features to establish a successful technology that enhances the desired function while minimizing the adverse effects in the environment. The goal of polymer nanoparticles in agriculture is to reduce the quantity of agrochemicals required and enhanced uptake of active ingredient and protect from degradation [41]. Owing to their characteristic functional groups, PNPs have potential ability for their enhanced ability in accumulation, controlled release behaviour and simple use. The uptake and translocation of agrochemicals by PNPs depend on surface charge, size and chemical nature. The degradation of PNPs can be attributed to chemical, physical or biological methods. The specific parameters such as pH, temperature, light exposure, enzymatic activity could provide the promising strategies for the PNP degradation. PNPs typically have low toxic effect on environment and are often reported to minimize the toxic effect of agrochemicals, presenting an extensive benefit in progressing the competence and safe use of active ingredient. However, PNPs showed slight change in activity of microbial interactions [37]. Current research reports suggest that PNPs pose minimal or short-term environmental hazards and are alleviated when compared to non-encapsulated formulations of agrochemicals. However, further studies are required to evaluate the potential toxicity and long-term soil studies of PNP degraded products.

Conclusions

To maintain the sustainability in agriculture field, researchers have been relied on nanotechnology. The basic principle of sustainability in agriculture is acquiring the minimisation of the agrochemicals with low production costs and higher outputs. In this context, nanocarriers with sustained release are the smart products for modern agriculture. The recent developments in PNP technology for the encapsulation of agrochemicals have promoted sustainable and successful formulations in agriculture. This review addressed the emergence of PNPs in agriculture for the encapsulation of agrochemicals that reduce undesirable toxic effects and enhance their stability. The properties of PNPs depend on design and method of polymerisation. Owing to this, various synthesis methods were explored in the article. The article

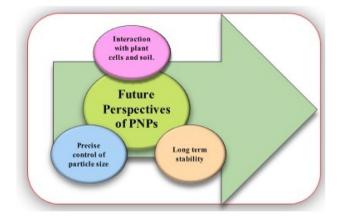


Fig. 2 Future perspectives of PNPs for well-defined strategic applications in the field of agriculture

also provides insights into nanoformulations of PNPs that endows the aspect of carriers of agrochemicals.

Future recommendations

The emergence of PNPs has provided the promising alternative to the conventional technologies in delivering agrochemicals. Figure 2 represents the future perspectives of PNPs for well-defined strategic applications in the field of agriculture. The field of PNP is still in blossoming stage and requires attention of researchers in the development of precise control of particle size and morphology as these are the key stimulus that determines the properties and applications. Work has to be done explicitly on the PNP interaction and their accumulation in plant cells. Exploration is still being done on applications of PNPs for safety assessment, evaluation standards and public concern issues. Additionally, the behaviour of PNPs containing agrochemicals with soil and water physic-chemical properties is to be further investigated. Finally, studies on long-term stability, effects of nanoparticles and product economics need to be addressed for the appropriate and realistic agricultural applications of PNPs.

Data availability No datasets were generated or analysed during the current study of review article.

Declarations

Conflict of interest We declare that the manuscript is submitted with the full knowledge and consent of all co-authors. The authors declare there is no conflict of interest.

References

- Adhikari C (2021) Polymer nanoparticles-preparations, applications and future insights: a concise review. Polym Plast Technol Mater 60(18):1996–2024. https://doi.org/10.1080/25740881.2021. 1939715
- Ammar AS (2018) Nanotechnologies associated to floral resources in agri-food sector. Acta Agronómica 67:146–159. https://doi.org/ 10.15446/acag.v67n1.62011
- Anton N, Benoit JP, Saulnier P (2008) Design and production of nanoparticles formulated from nano-emulsion templates—a review. J Control Release 128:185–199
- Ashfaq M, Talreja N, Chuahan D, Srituravanich W (2019) Polymeric nanocomposite-based agriculture delivery system: emerging technology for agriculture. In: Genetic engineering—a glimpse of techniques and applications. IntechOpen. https://doi. org/10.5772/intechopen.89702
- Bohidar H, Rawat K (2017) Design of nanostructures: selfassembly of nanomaterials, 2st edition. In: Biopolymeric nanoparticles, pp 293–324
- Campbell BM, Thornton P, Zougmore R, Asten PV, Lipper L (2014) Sustainable Intensification: what is its role in climate smart agriculture? Curr Opin Environ Sustain 8:39–43. https:// doi.org/10.1016/j.cosust.2014.07.002
- Chaud M, Souto EB, Zielinska A (2021) Nanopesticides in agriculture: benefits and challenge in agricultural productivity, toxicological risks to human health and environment. Toxics 9(6):131. https://doi.org/10.3390/toxics9060131
- Chauhan N, Dilbaghi N, Gopal M, Kumar R, Kim KH, Kumar S (2017) Development of chitosan nanocapsules for the controlled release of hexaconazole. Int J Biol Macromol 97:616–624. https://doi.org/10.1016/j.ijbiomac.2016.12.059
- Crespy D, Landfester K (2010) Miniemulsion polymerization as a versatile tool for the synthesis of functionalized polymers. Beilstein J Org Chem 6:1132–1148. https://doi.org/10.3762/ bjoc.6.130
- Delaney J, Clarke E, Hughes D, Rice M (2006) Modern agrochemical research: a missed opportunity for drug discovery? Drug Discov Today 11(17–18):839–845. https://doi.org/10.1016/j.drudis. 2006.07.002
- 11. Detsi A et al (2020) Nanosystems for the encapsulation of natural products: the case of chitosan biopolymer as a matrix. Pharmaceutics 12(7):669. https://doi.org/10.3390/pharmaceutics12070669
- Duran N, Marcato PD (2013) Nanobiotechnology perspectives. role of nanotechnology in the food industry: a review. Int J Food Sci Technol 48:1127–1134. https://doi.org/10.1111/ijfs.12027
- Feng BH, Peng LF (2012) Synthesis and characterization of carboxymethyl chitosan carrying ricinoleic functions as an emulsifier for azadirachtin. Carbohydr Polym 88:576–582
- Fessi H, Puisieux F, Devissaguet JP, Ammoury N, Benita S (1989) Nanocapsule formation by interfacial polymer deposition following solvent displacement. Int J Pharm 55:R1-4
- Ganachaud F, Katz JL (2005) Nanoparticles and nanocapsules created using the ouzo effect: spontaneous emulsification as an alternative to ultrasonic and high-shear devices. ChemPhysChem 6:209–216
- Grillo R, Leonardo FF, Monica JBA, Janeck JSF, Reinhilde S, Qasim C (2020) Ecotoxicological and regulatory aspects of environmental sustainability of nanopesticides. J Hazard Mater 404:124148. https://doi.org/10.1016/j.jhazmat.2020.124148
- Hack B, Egger H, Uhlemann J, Henriet M, Wirth W, Vermeer-AWP DD (2012) Advanced agrochemical formulations through encapsulation strategies? Chem Ing Tec 84(3):223–234. https:// doi.org/10.1002/cite.201100212

- Hanemann T, Szabo DV (2010) Polymer-nanoparticle composites: from synthesis to modern applications. Materials (Basel) 3(6):3468–3517
- Ivar V, Arzoomand NS, Boqvist S (2020) Food security, safety, and sustainability—getting the trade-offs right. Front Sustain Food Syst 4:16. https://doi.org/10.3389/fsufs.2020.00016
- Jana P, Shyam M, Singh S, Jayaprakash V, Dev A (2021) Biodegradable polymers in drug delivery and oral vaccination. Eur Polym J 142:110. https://doi.org/10.1016/j.eurpolymj.2020. 110155
- Kaarunya S, Tan KX, Loo SCJ (2020) Developing nano-delivery systems for agriculture and food applications with nature-derived polymers. iScience 23(5):101055. https://doi.org/10.1016/j.isci. 2020.101055
- Kamaly N, Yameen B, Wu J, Farokhzad OC (2016) Degradable controlled-release polymers and polymeric nanoparticles: mechanisms of controlling drug release. Chem Rev 116:2602–2663
- Kanwar R, Rathee J, Patil MT, Mehta SK (2018) Microemulsions as nanotemplates: a soft and versatile approach. In: Microemulsion—a chemical nanoreactor. IntechOpen. https://doi.org/ 10.5772/intechopen.80758
- 24. Kawashima Y (2001) Nanoparticulate systems for improved drug delivery. Adv Drug Deliv Rev 47:1–2
- 25. Kim E, Yang J, Choi J, Jin-Suck S, Yong-Min H, Haam S (2009) Synthesis of gold nanorod-embedded polymeric nanoparticles by a nanoprecipitation method for use as photothermal agents. Nanotechnology 20:365602
- 26. Krishnamoorthy K, Mahalingam M (2015) Selection of a suitable method for the preparation of polymeric nanoparticles: multi-criteria decision making approach. Adv Pharm Bull 5(1):57–67. https://doi.org/10.5681/apb.2015.008
- Kumar S, Kumar D (2017) Preparation, characterization, and bio-efficacy evaluation of controlled release carbendazim-loaded polymeric nanoparticles. Environ Sci Pollut Res 24(1):926–937
- Kumera N, Ayman N, Siraj U, Yetenayet BT (2021) Application of nanotechnology in agriculture, postharvest loss reduction and food processing: food security implication and challenges. Heliyon 7(12):e08539. https://doi.org/10.1016/j.heliyon.2021.e08539
- Leslie RS, Adisa IO, Liu B, Elmer WH, White JC, Dimkpa CO, Fairbrother DW (2021) Biodegradable polymer nanocomposites provide effective delivery and reduce phosphorus loss during plant growth. ACS Agric Sci Technol 1(5):529–539. https://doi.org/10. 1021/acsagscitech.1c00149
- Li T, Lu S, Yan J, Bai X, Gao C, Liu M (2019) An environment-friendly fertilizer prepared by layer-by-layer self-assembly for pH-responsive nutrient release. ACS Appl Mater Interfaces 11:10941–10950. https://doi.org/10.1021/acsami.9b01425
- Liu G, Liu P (2010) Synthesis of monodispersed crosslinked nanoparticles decorated with surface carboxyl groups via soapless emulsion polymerization. Colloid Surf A 354:377–381
- Lu Y, Sah KW, Xu J (2017) Synthesis, morphologies and building applications of nanostructured polymers. Polymers (Basel) 9(10):506. https://doi.org/10.3390/polym9100506
- Mandal T, Fleming M, Walt D (2002) Preparation of polymer coated gold nanoparticles by surface-confined living radical polymerization at ambient temperature. Nano Lett. https://doi. org/10.1021/nl015582c
- Maraveas C (2020) Production of sustainable and biodegradable polymers from agricultural waste. Polymers 2020(12):1127. https://doi.org/10.3390/polym12051127
- Margulis-Goshen K, Magdassi S (2012) Nanotechnology: an advanced approach to the development of potent insecticides. In: Ishaaya I, Horowitz AR, Palli SR (eds) Advanced technologies for managing insect pests. Springer, Dordrecht, pp 295–314

- Maricarmen IM, Ragazzo-Sánchez JA, Calderón-Santoyo M (2021) An extensive review of natural polymers used as coatings for postharvest shelf-life extension: trends and challenges. Polymers (Basel) 13(19):3271. https://doi.org/10.3390/polym13193 271
- 37. Maruyama CR, Guilger M, Pascoli M, Bileshy-José N, Abhilash PC, Fraceto LF, De Lima R (2016) Nanoparticles based on chitosan as carriers for the combined herbicides imazapic and imazapyr. Sci Rep 6:19768. https://doi.org/10.1038/srep19768
- Maruyama CR et al (2015) Nanoparticles based on chitosan as carriers for the combined herbicides imazapic and imazapyr. Sci Rep 6:1–15
- Mei QS, Lau WJ, Goh PS, Tseng HH, Wahab RA, Ismail AF (2020) Progress of interfacial polymerization techniques for polyamide thin film (nano) composite membrane fabrication: a comprehensive review. Polymers 12(12):2817. https://doi.org/10. 3390/polym12122817
- Messa LL, Faez R (2020) Spray-dried chitosan/nanocellulose microparticles: synergistic effects for the sustained release of NPK fertilizer. Cellulose. https://doi.org/10.1007/s10570-020-03482-2
- Mittal D, Kaur G, Singh P, Yadav K, Ali SA (2020) Nanoparticlebased sustainable agriculture and food science: recent advances and future outlook. Front Nanotechnol 2:579954. https://doi.org/ 10.3389/fnano.2020.579954
- Monteiro M, Cunningham M (2012) Polymer nanoparticles via living radical polymerization in aqueous dispersions: design and applications. Macromolecules 45(12):4939–4957. https://doi.org/ 10.1021/ma300170c
- 43. Nguyen CA, Allemann E, Schwach G, Doelker E, Gurny R (2003) Synthesis of a novel fluorescent poly(d, l-lactide) end-capped with 1-pyrenebutanol used for the preparation of nanoparticles. Eur J Pharm Sci 20:217–222
- Ngwuluka NC, Abu-Thabit NY, Uwaezuoke OJ, Erebor JO, Ilomuanya MO, Mohamed RR, Ebrahim NA (2021) Natural polymers in micro-and nanoencapsulation for therapeutic and diagnostic applications: part II—polysaccharides and proteins. Nano Microencapsul Tech Appl 8:9. https://doi.org/10.5772/intechopen. 95402
- 45. Park EJ, Erdem T, Ibrahimova V, Nizamoglu S, Demir H, Tuncel D (2011) White-emitting conjugated polymer nanoparticles with cross-linked shell for mechanical stability and controllable photometric properties in color-conversion LED applications. ACS Nano 5(4):2483–2492. https://doi.org/10.1021/nn103598q
- Patra JK, Das G, Fraceto LF et al (2018) Nano based drug delivery systems: recent developments and future prospects. J Nanobiotechnol 16(1):71. https://doi.org/10.1186/s12951-018-0392-8
- 47. Pereira AES, Grillo R, Mello NFS, Rosa AH, Fraceto LF (2014) Application of poly(epsilon-caprolactone) nanoparticles containing atrazine herbicide as an alternative technique to control weeds and reduce damage to the environment. J Hazard Mater 268:207–215
- Perez JJ, Francois NJ (2016) Chitosan-starch beads prepared by ionotropic gelation as potential matrices for controlled release of fertilizers. Carbohydr Polym 148:134–142. https://doi.org/10. 1016/j.carbpol.2016.04.054
- Pérez-de-Luque A, Rubiales D (2009) Nanotechnology for parasitic plant control. Pest Manag Sci 65:540–545
- Perlatti B, Bergo PLS, Fernandes MGMF, Forim MR (2013) Insecticides-development of safer and more effective technologies. In: Trdan S (ed) InTech: Rijeka, pp 523–550
- 51. Peteu SF, Oancea F, Sicuia OA, Constantinescu F, Dinu S (2010) Responsive polymers for crop protection. Polymers 2:229–251
- PineiroV AJ, Durr J et al (2020) A scoping review on incentives for adoption of sustainable agricultural practices and their outcomes. Nat Sustain 3:809–820. https://doi.org/10.1038/ s41893-020-00617-y

- Prasad R, Bhattacharyya A, Nguyen QD (2017) Nanotechnology in sustainable agriculture: recent developments, challenges, and perspectives. Front Microbiol 8:1014. https://doi.org/10.3389/ fmicb.2017.01014
- Prasad R, BhattacharyyaA NQD (2017) Nanotechnology in sustainable agriculture: recent developments, challenges, and perspectives. Front Microbiol 8:1–13. https://doi.org/10.3389/fmicb. 2017.01014
- Pulingam T, Foroozandeh P, Chuah J-A, Sudesh K (2022) Exploring various techniques for the chemical and biological synthesis of polymeric nanoparticles. Nanomaterials 12(3):576. https://doi. org/10.3390/nano12030576
- Shakiba S, Carlos EA, Sachin P, Cristina MS, Debora FR, Stacey ML (2020) Emerging investigator series: polymeric nanocarriers for agricultural applications: synthesis, characterization, and environmental and biological interactions. Environ Sci Nano 7:37–67. https://doi.org/10.1039/C9EN01127G
- 57. Shang Q, Shi Y, Zhang Y, Zheng T, Shi H (2013) Pesticideconjugated polyacrylate nanoparticles: novel opportunities for improving the photostability of emamectin benzoate: pesticideconjugated polyacrylate nanoparticles. Polym Adv Technol 24:137–143. https://doi.org/10.1002/pat.3060
- Shang Y, Hasan MK, Ahammed GJ, Li M, Yin H, Zhou J (2019) Applications of nanotechnology in plant growth and crop protection: a review. Molecules 24(14):2558. https://doi.org/10.3390/ molecules24142558
- Shang Q, Shi Y, Zhang Y, Zheng T, Shi H (2013) Pesticide-conjugated polyacrylate nanoparticles: novel opportunities for improving the photostability of emamectin benzoate: pesticide-conjugated polyacrylate nanoparticles. Polym Adv Technol 24:137–143
- Shao C, Zhao H, Wang P (2022) Recent development in functional nanomaterials for sustainable and smart agricultural chemical technologies. Nano Convergen 9:11. https://doi.org/10.1186/ s40580-022-00302-0
- Sikder A, Amanda KP, Sam JP, Richard N, Rachel KOR (2021) Recent trends in advanced polymer materials in agriculture related applications. ACS Appl Polym Mater 3:1203–1217. https://doi. org/10.1021/acsapm.0c00982
- 62. Singh MN, Hemant KS, Ram M, Shivakumar HG (2010) Microencapsulation: a promising technique for controlled drug delivery. Res Pharm Sci 5(2):65–77
- Song Y, Fan JB, Wang S (2017) Recent progress in interfacial polymerization. Mater Chem Front 8:9. https://doi.org/10.1039/ c6qm00325g

- Suganya V, Anuradha V (2017) Microencapsulation and nanoencapsulation: a review. Int J Pharmaceut Clin Res 9:233–239. https://doi.org/10.25258/ijpcr.v9i3.8324
- 65. Sun C, Shu Ke, Wang W, Ye Z, Liu T, Gao Y, Zheng H, He G, Yin Y (2014) Encapsulation and controlled release of hydrophilic pesticide in shell cross-linked nanocapsules containing aqueous core. Int J Pharm 463(1):108–114
- 66. Timilsena Y, Haque M, Adhikari B (2020) Encapsulation in the food industry: a brief historical overview to recent developments. Food Nutr Sci 11:481–508. https://doi.org/10.4236/fns.2020. 116035
- 67. Tong Y, Wu Y, Zhao C, Xu Y, Lu J, Xiang S et al (2017) Polymeric nanoparticles as a metolachlor carrier: water-based formulation for hydrophobic pesticides and absorption by plants. J Agric Food Chem 65:7371–7378. https://doi.org/10.1021/acs.jafc.7b021 97
- Tong Y, Wu Y, Zhao C, Xu Y, Lu J, Xiang S, Zong F, Wu X (2017) Polymeric nanoparticles as a metolachlor carrier: waterbased formulation for hydrophobic pesticides and absorption by plants. J Agric Food Chem 65:7371–7378
- Vanderhoff JW, El Aasser MS, Ugelstad J (1979) Polymer emulsification process. US Patent 4,177,177
- Wang L, Qin X, Miao X, Chen H, Zhou Y, Cai A (2020) Synthesis and non-destructive detailed structure characterization of carboxymethyl xylan from bagasse. J Carbohydr Chem 39:131–144. https://doi.org/10.1080/07328303.2020.1748643
- Zhang J, Li M, Fan T, Xu Q, Wu Y, Chen C, Huang Q (2013) Construction of novel amphiphilic chitosan copolymer nanoparticles for chlorpyrifos delivery. J Polym Res 20:1–11
- 72. Zweers MLT, Engbers GHM, Grijpma DW, Feijen J (2006) Release of anti-restenosis drugs from poly(ethylene oxide)poly(dl-lactic-coglycolic acid) nanoparticles. J Control Rel 114:317–324

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Springer Nature or its licensor (e.g. a society or other partner) holds exclusive rights to this article under a publishing agreement with the author(s) or other rightsholder(s); author self-archiving of the accepted manuscript version of this article is solely governed by the terms of such publishing agreement and applicable law.