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Utilization of biodegradable carrier-based nano herbicide formulations for sustainable weed management in agriculture

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Recently, the injudicious use of herbicides in agriculture is causing numerous hazards that affect the environment and living organisms. To achieve the SDG 2030 agenda goal 12- "Ensure sustainable consumption and production patterns," there is an urgent need to shift towards using toxic-free agricultural inputs. Various techniques are widely adopted to control weed growth and development, but farmers mostly rely on herbicide application. Nanotechnology-enabled herbicide formulations are more sustainable and efficient in weed control than traditional sources. The nanoherbicides enable lesser application frequency and minimum quantity requirement, thereby preventing herbicide accumulation in soil and water bodies. Mainly nano-mediated biodegradable carrier-based herbicides possess properties of prolonged release, targeted inhibition, reduced mobility in soil, better adhesion to the plant surface, and retards rapid degradation of active ingredients (AIs), which increase herbicide use efficiency against weeds. Biodegradable carrier materials are cost-effective and readily available from living/non-living organisms and mineral sources, which can be an alternate source for metal/metal-oxide carrier materials. Materials like chitosan, plant derivatives, clay particles, and synthetic polymers are notable carrier materials reported for encapsulating or loading herbicide molecules. Applying nano-mediated herbicides is an innovative methodology for controlling weeds while considering environmental safety. This review focused mainly on recent advances in biodegradable carrier-based herbicide application in agriculture to mitigate the crisis in sustainable weed management. The ultimate objective of this manuscript is to serve as a source of reference material for exploring the nano-based herbicide formulations, their mobility, fate, and future perspectives.

KEYWORDS

nanotechnology, herbicide, biodegradable, weed, encapsulation, slow-release, sustainable, carrier-based

1 Introduction

The global population is projected to increase from over 7 billion to 8.7 billion by 2033, which is expected to directly impact the per capita food consumption (OECD/FAO, 2024). The increasing demand for food production needs better utilization of natural and renewable resources (Fraceto et al., 2016). To mitigate the food demand, agriculture is demanding the application of more inputs, including fertilizers and pesticides. Weeds are renowned for their competitive behavior in agriculture, resulting in yield losses. Therefore, weed management is an essential inter-cultivation practice during crop production. Agriculture often faces challenges in managing the use of plant protection chemicals. Nevertheless, weeds account for the highest proportion of production loss among all other pests in agriculture, with an average yield loss of 34% (Jabran et al., 2015). Crop-weed competition is prevalent in agriculture, and it diminishes the yield of crops (Campos et al., 2023). The foremost cause of competitiveness is the weed's interest in resources such as light, water, and nutrients (Singh et al., 2022).

Herbicides are a type of formulation that falls under the pesticide category (Periakaruppan et al., 2023; Rajput et al., 2021), which are described as any substance that is used to prevent, destroy, or inhibit the growth of weeds, mainly in agricultural lands (Paul et al., 2024). In 2023, global agricultural pesticides consumption rates were as follows: herbicides > fungicides and bactericides > insecticides > others, with an amount of 1732.3, 816.38, 757.54, and 220.15 thousand metric tons (FAO, 2023). Herbicides are chemical compounds derived from synthetic or naturally available substances. Herbicides are motivated to control or inhibit weed growth in the crop circumstance, which has resulted in a reliable source of controlling weeds, alongside causing anthropogenic pollution such as degrading soil fertility, water, and air quality (Singh et al., 2023; Verma et al., 2022).

Herbicide application in greenhouses and open fields is common in agriculture, leading to occupational exposure among workers (Sameeha, 2023; Abdollahdokht et al., 2022). Herbicides applied, either foliar or soil, may undergo leaching, volatilization, and runoff, affecting biodiversity (Wilms et al., 2020). Unfortunately, it accumulates in soil and water bodies and reaches the food chain, which can cause hazards to human life and the environment for several years (Ghazi et al., 2023).

Abbreviations: UV-vis, Ultraviolet-visible spectra; ATZ, Atrazine; AI, Active ingredient; DLS, Dynamic light scattering; NTA, Nanoparticle tracking analysis; AFM, Atomic force microscopy; UHPLC, Ultra-High Performance Liquid Chromatography; HPLC, High-Performance Liquid Chromatography; NP, Nanoparticles; XRD, X-ray diffraction analysis; TEM, Transmission electron microscopy; SEM, Scanning electron microscopy; EDX, Energy Dispersive X-ray spectroscopy; PBAT, Poly (butylene adipate-co-terephthalate); PCL, Poly (epsilon-caprolactone); PAA HCL, Polyallyl amine hydrochloride; PLGA, Poly (lactic-co-glycolic acid); PLA, Polylactic acid; PVA, Polyvinyl alcohol; PMMA, Poly (methyl methacrylate); XPS, X-ray photoelectron spectroscopy; PEG, Polyethylene glycol; ROS, Reactive Oxygen Species; LDH, Layered Double Hydroxide; NMR, Nuclear Magnetic Resonance spectroscopy; CRM, Controlled release mechanism; FDA, Food and Drug Administration.

Herbicides such as 2,4-D, oxyfluorfen, glyphosate, atrazine, diuron, tebuthiuron, alachlor, metribuzin, fenuron, monuron, metolachlor, fluometuron, and ametryn are reported as water pollutants in several research findings (Brillas, 2021). For instance, glyphosate is one of the most widely used herbicides throughout the world, and it is identified as an essential factor causing various illnesses such as cancer, autism, infertility, depression, Alzheimer's, Parkinson's, and obesity in human society (Anarghou et al., 2024). The herbicides were found to be causing detrimental effects through biological magnification and long-term residual buildup in the ecosystem (Ebube et al., 2024). On the other hand, the target organism does not fully utilize the applied chemical because of various external factors. Over 90% of pesticides, including herbicides, insecticides, and fungicides, are going unutilized after application (Paul et al., 2024). To overcome this peril, the United Nations stipulated its third goal in the SDG 2030 agenda to reduce the disorders caused by chemical contamination in living circumstances (Onyeaka et al., 2024).

In a recent field experiment, the herbicide residue in the post-harvest soil was investigated. When four herbicides (triasulfuron, clopyralid, pyroxasulfone, and chlorsulfuron) were applied to the wheat crop at the mid-tillering stage, the number of nodules, root length, shoot length, and whole plant weight decreased in subsequently cultivated pasture and legume crops (Yates et al., 2024).

In agriculture, synthetic herbicides are considered a cost-effective and efficient method of weed control. But the herbicide resistance is also one of the worries brought by the new generation of herbicides (Kumar et al., 2017). There are 533 herbicide-resistant cases, with 273 weed species (156 dicots and 117 monocots) reported to 168 different herbicides. According to the HRAC (Herbicide Resistance Action Committee), 34 herbicide groups were classified based on mechanisms of action. To support this certainty, a survey has been reported, where the resistance to herbicides has the highest share of 54% in the *Poaceae* family, followed by *Brassicaceae* and *Asteraceae* with 30% (Oreja et al., 2024). Figure 1 depicts the recent data on herbicide resistance that occurs worldwide due to the overuse of herbicides. In a broader sense, herbicide production without a new mode of action will be prone to herbicide resistance in various weed species (Khan et al., 2024). Target-site resistance (TSR) and non-target-site resistance (NTSR) are two mechanisms responsible for resistance in most weed biotypes (Sen et al., 2023). At higher levels, both TSR and NTSR mechanisms can sometimes combine and produce survival mechanisms at an individual level or within a population. In addition, herbicide resistance in a trait is acquired through the pollination nature of the weed species. Notably, different resistance mechanisms to single or multiple herbicides can be present in cross-pollinated weed groups; this process occurs rapidly in cross-pollinated groups compared with self-pollinated groups (Gaines et al., 2020).

TSR mechanism occurs mainly due to 1) gene mutation affecting the herbicide binding site at single or multiple protein targets polymorphism, 2) codon deletion, and 3) gene duplication. NTSR is more complex than TSR in terms of mechanisms of action, including reduced translocation, adsorption, more sequestration,

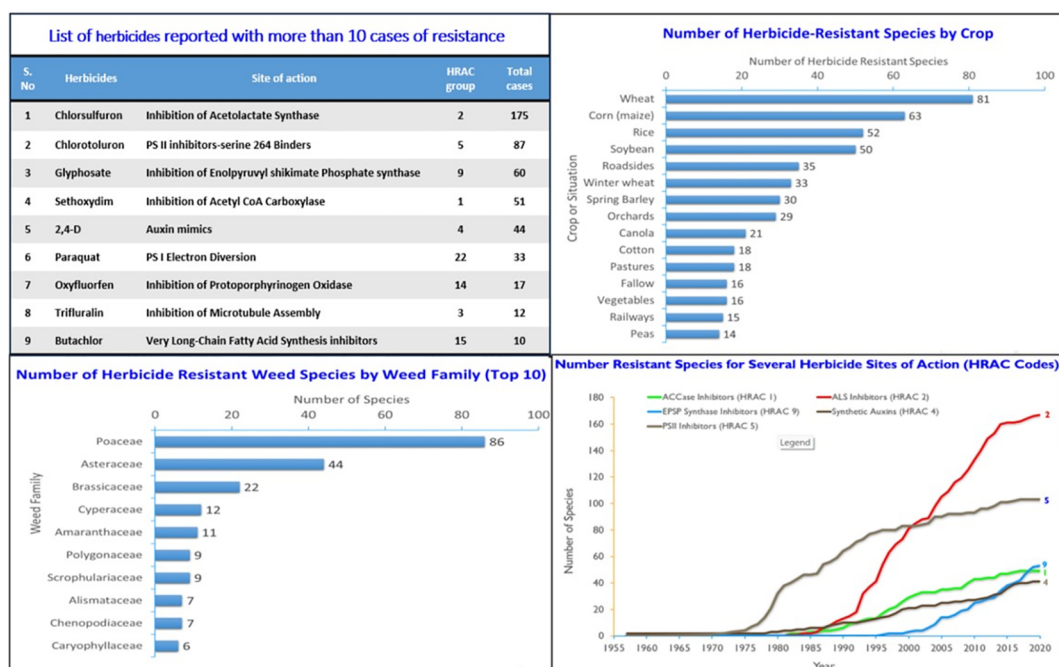


FIGURE 1

Data on herbicide-resistant weed species sourced from the international survey of herbicide-resistant weeds (Source: Heap I. The International Herbicide-Resistant Weed Database. www.weedscience.org).

and metabolic degradation. Generally, herbicide efficacy depends on the quantity of herbicide that enters a plant cell and how long it reacts with the target site. GSH S-transferases, cytochromes P450, aryl acylamidase, glucosyl, and other enzymes cause herbicide metabolism (produce noninhibitive by-products) resulting in herbicide resistance (Gaines et al., 2020). The sustainable bioactive chemical release and targeted inhibition of nano-enabled molecules remain long-term in the crop environment. This leads to avoiding frequent herbicide application, which subsequently reduces weed resistance. Hence, the diverse resistance mechanism of weeds can be mitigated by applying nanoherbicides.

After the green revolution, pesticides emerged as an inevitable component of agriculture, but concealing considerable complications in pesticide use must be redefined (Shangguan et al., 2024). Consuming tainted food and water with pesticide residues impacts the general public. These constraints indicate the need for intelligent, responsive, biodegradable, and biocompatible alternatives (Abdollahdokht et al., 2022). Nanotechnology is approved to be a novel technology that can revitalize the farming system and food production. Numerous uses of nanotechnology have been found in various domains, including chemical production, engineering, energy, clothing, beauty care, medical science, material science, food, and agriculture (Khan et al., 2022; Paul et al., 2024).

Combining herbicide molecules with nanoparticles (NPs) increases efficiency by up to 84% (Rajput et al., 2021). Nanotechnology in agriculture is becoming a component of “Precision farming” and “Sustainable agriculture” owing to its

priority of increasing food production, with more focus on environmental safety (He et al., 2019). To maximize the crop yield, nanoparticles, and nanocomposite-enabled crop protection agrochemicals provide the advantages of controlled release and increased use efficiency against pests and diseases (Abd-Elsalam, 2024).

Nanotechnology-enabled agriculture practices can be considered a forthcoming green revolution, with reduced threats caused by the contemporary green revolution (Kumar, 2020). Nanotechnology in agriculture involves the production of nano-size inputs in the range of 1-100 nm materials for tackling agricultural constraints and global food shortages (Campos et al., 2023; Lv et al., 2023). The synonym of “nano” is one-billionth of a meter (Nuruzzaman et al., 2019), roughly 1/80,000 the size of a human hair diameter, or approximately the size of 10 hydrogen atoms (Paul et al., 2024). To achieve sustainability, targeted delivery and dose reduction could be an effective approach (Khan et al., 2024; Gayathri et al., 2023). Nano-based biodegradable herbicides open the window for mitigating concerns about controlling weeds on the agricultural field sustainably. Recently, several benefits of polymeric carriers have been studied extensively in the biomedical field to develop drug delivery systems (MaChado et al., 2022).

In agriculture, polymeric nanocarriers are underutilized, and their applications have been explored less in weed control. However, the commercial availability of carrier-based nanoherbicides is less prevalent. The high production cost for perfect infrastructure and lack of multidisciplinary approach in laboratory research with multiple field trials. Thus, nanoherbicide application in agriculture has opened up wider research opportunities in the current decade.

2 Nanoherbicide- an alternative to conventional herbicide

Nano-herbicides are specially fabricated herbicides, and the AI molecules are coated or loaded with nano-size (1-100 nm) carrier materials (Paul et al., 2024). Innovation of new agricultural methods and technologies is a highly paid priority among the global communities to discard hunger and malnutrition (Food and Agriculture Organization., 2018; Xin et al., 2020). Figure 2 represents the chronological evolution of herbicides over the years. In numerous studies, conventional herbicides have demonstrated low water solubility and inconsistent release kinetics. It directs farmers to apply more chemicals in agricultural fields, which leads to high application costs, herbicide resistance, and toxicity buildup in the ecosystem. On the other hand, nano-enabled herbicide delivery writes off pollution concerns and minimizes labor costs for herbicide application with a lesser quantity (An et al., 2022).

Nano-enabled herbicides reduce the overall requirement for herbicide quantity owing to the extended-release of AI molecules without undergoing external losses (de Oliveira et al., 2015; Zargar et al., 2023). Nanoencapsulated atrazine, clodinafop propargyl, and fenoxaprop-p-ethyl used at 10-fold less quantity on weeds provide similar results to commercial formulations (Khan et al., 2022). Nano-encapsulated herbicides obtain a high surface area and subsequently require much less active compounds in their primary field application (Kremer, 2019). Applying nanotechnology-intervened encapsulated herbicide formulations increases weed control efficiency and reduces environmental threats (Kah and Hofmann, 2014). The higher surface area of the particle to the lesser volume ratio guarantees the NPs a powerful carrier tool and makes them a vector for bioactive molecules (Xin et al., 2020).

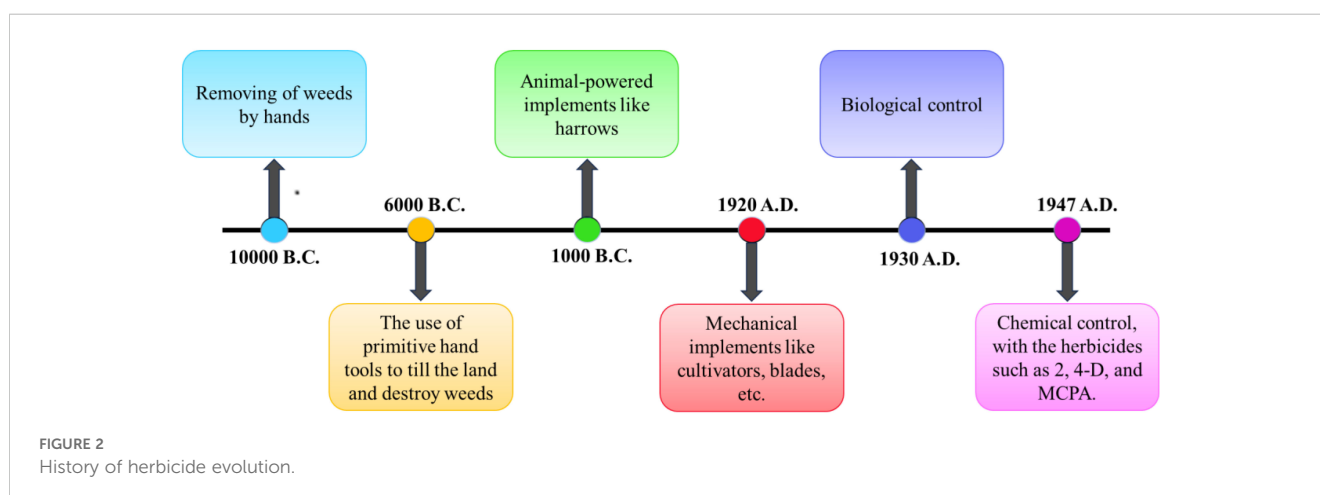
Nano-herbicides are specifically engineered to tackle several limitations, such as evaporation, volatilization, leaching, runoff, erosion, photochemical degradation, and microbial and chemical degradation (An et al., 2022; Paul et al., 2024). The wettability and dispersibility of herbicide formulations are enhanced when herbicides are loaded into nanomaterials containing a high specific surface area and minute herbicidal active ingredients (AI)

(Forini et al., 2022; Manisankar et al., 2022). To optimize the herbicidal effects of nanoherbicides over traditional herbicides, the primary focus of their fabrication is on improving their physiochemical features, such as size, shape, surface chemistry, concentration, etc. The chemical makeup of the nanomaterials determines the interaction of nanoherbicides with weed foliage, roots, and seeds (Forini et al., 2022).

According to the properties and chemical constituents of carrier materials, nanoherbicides are divided into three types: organic, inorganic, and hybrid-based (Forini et al., 2022). Organically available carrier materials such as proteins, lipids, lignocellulosic materials, clays, etc (Su et al., 2019). possess easy degradability, better stability, bio-efficacy, easy availability, and feasibility. The encapsulation technique driven through biodegradable polymers offers various benefits, including enhanced efficacy, sustainable biological compound release, environmental factor protection (Sahoo et al., 2022), and self-life of materials (An et al., 2022; Campos et al., 2023).

On the other hand, metal and metal oxide NPs act as carrier materials for delivering AI molecules owing to their high surface area, higher reactive ability, and optical and electronic properties (Xin et al., 2020). However, the pristine metallic NPs pose negative impacts, such as unaddressed environmental hazards and health risks to organisms (Lead et al., 2018). Even though metal NPs have the potential to act as carrier materials, they exhibit a wide range of toxicity threats in the ecosystem. For example, foliar application of metallic NP suspension (10 to 1000 ppm) resulted in the accumulation of metal NP content in plant (root and shoot) parts ranging from 10 to 70 mg/kg of dry weight (Su et al., 2019). In conventional agrochemicals, currently accessible carrier materials are derived from petroleum, such as polyurea and polyolefins, exhibiting notable resistance to degradation. Consequently, this characteristic leads to the buildup of detrimental substances within the biogeochemical cycle (MaChado et al., 2022).

Hybrid nanoherbicides are different nanomaterials in a single structure with herbicide molecules. Hybrid nanomaterials contain agrochemicals with two or more carrier materials like natural polymers, fabricated polymers, and inorganic NPs (Khan et al., 2022). Combining the potential chemical interaction of different



nanomaterials turns them into outstanding carrier materials. Hybrid nanomaterials promote traceability, targetability, and stimuli-responsive properties like organic and inorganic types. Thus, hybrid nanomaterials pose an excellent source of carrier materials for better affinity and spreadability with plant surfaces and ensure sustained release with a reduced chance of UV irradiation degradation (Forini et al., 2022). Completely biomass-based hybrid materials constitute xylan, starch, cellulose, lignin, etc. For example, a study reported that hybrid xylan-lignin nanomaterials have core-shell structure and amphiphilic properties (Jiang et al., 2020). Natural clay (inorganic mineral) and biopolymers are compatible after making chemical alterations and act as carriers for herbicide molecules (Granetto et al., 2022). Further, the release kinetic and weed control abilities were discussed briefly in the upcoming section of the review.

Since the carrier material's biodegradability is a high priority among the available sources, we have reviewed recently published biodegradable carrier-based nano herbicide applications for weed control in agriculture in the upcoming sections. Naturally available or synthetically produced biodegradable polymers such as chitosan and alginates are synthesized by the assembly of copolymers, which are scientifically proven to be eco-friendly biopolymers (Muthukrishnan et al., 2019).

Managing weed flora through administering nano-mediated herbicides is perfectly compatible with its controlled-release mechanism (CRM) (Kumar et al., 2017; Paul et al., 2024) and reduces phytotoxicity in the crop ecosystem. For example, crosslinking substances like glutaraldehyde or genipin can enhance the structural integrity and stability of chitosan NPs, ensuring the controlled release of herbicide molecules (Thambiliyagodage et al., 2023). The CRM was ensured by adsorbing, attaching, entrapping, or encapsulating the AI with organic and inorganic nano-based carrier materials (Paul et al., 2024). Furthermore, optimized diuron nanoformulation (ODNF) was synthesized using subabul stem lignin as a matrix for the controlled release of herbicides. The polymer matrix greatly influences the release kinetics and bioefficacy (weed control) of the AI molecules. Notably, the release of diuron was observed under HPLC in all the pH levels (acidic-5.0, neutral-7.0, and basic- 9.0). The ODNF results in a nonlinear biphasic release of AI from the matrix, indicating that initial burst release is followed by controlled release until the 120th day. The release rate was highly influenced by the pH, where the acidic pH was slower than the neutral and basic pH, released at 53%, 62.2%, and 67%, respectively. The initial fast release is due to the diffusion of herbicide molecules from the periphery of the outer matrix. In contrast, the subsequent slow release in a while is due to an increase in diffusion distance towards the inner core of the matrix (presence of diffused herbicide molecule in the depleted zone). This result provides insights into CRM occurrence in the nano-enabled herbicide molecules without compromising weed control (Yearla and Padmashree, 2016). For instance, traditional herbicides are less effective in dryland conditions (Sahoo et al., 2022) due to the dormant weed seed bank in the subsurface soil. If the weed seed gets optimum moisture for its germination, the nondegraded nanoencapsulated herbicide molecules in the soil can restrict its growth and development.

Nanoformulations such as nano-encapsulation, nano-gels, nano-emulsions, etc., have better efficacy of AI molecules and pledge environmental safety (Abdollahdokht et al., 2022). The primary objectives of nano-encapsulation are controlled release and stimulus-responsive release (Ananikov, 2019; Xin et al., 2020). Nano-encapsulated pesticides are developed to promote the smart release (Gomollón-Bel, 2019) of AI molecules under biotic (plant pathogens, insects, and weeds) and abiotic (drought, soil texture, flooding, sunlight, temperature, and salinity) stresses. For instance, paraquat (PQ) is a widely used herbicide that binds to the photosystem I (PSI) site and inhibits electron transport to nicotinamide adenine dinucleotide phosphate (NADP⁺). PQ exposure to humans is highly toxic and causes acute ingestion, and chronic exposure leads to severe health problems. The compatible, user-friendly, photosensitive PQ formulation was loaded with supramolecular vesicles. The supramolecular vesicles were formulated using hydrophobic PQ as an inner core coated with two hydrophilic layers of an azobenzene derivative, and cucurbit[8]uril forms a 1:1:1 ternary complex. Under sunlight and UV irradiation, the azobenzene derivative changes its *trans*- to its *cis*-form, resulting in ternary complex dissociation. Furthermore, the formulation ensures the slow release of AI molecules and suppresses the invasive weed species (*Estuca arundinaceae*), similar to the free PQ. In addition, an *in vivo* study on the zebrafish and mouse model ensures an enhanced safety profile of the herbicide formulation (Gao et al., 2018).

Herbicides are lost in several ways, such as volatilization, vapor drift, and leaching of AIs. In most cases, the herbicides undergo volatilization after immediate application to the target area. Subsequently, drift happens due to wind blowing, and low soil adsorption causes the leaching of herbicide molecules. Nanohydrogels are a particular type of formulation that offers a variety of applications for agrochemicals with higher use efficiency and environmental sustainability. The high stability and low solubility of the formulation ensure the sustainable release of AIs and inhibit the target pest without affecting the other organisms (Kashyap et al., 2015; Ghaderpoori et al., 2020; Artusio et al., 2021). The mini emulsion template was formulated using sunflower oil, where the hydrophilic dicamba herbicide was loaded/encapsulated with alginate nanoparticles to form nanohydrogels. The presence of biocompatible sunflower oil and alginate NPs overcomes premature degradation of AIs. In addition, it acts as a toxic-free surfactant to reduce surface tension and as an adjuvant to improve plant uptake (Artusio et al., 2021). Similarly, using the ionic gelification method, chitosan-paraquat (PQ) encapsulated nanohydrogels were produced using sodium triphosphate and xanthan crosslinkers. The above studies resulted in the slow release of herbicide molecules and enhanced herbicidal efficacy (Ghaderpoori et al., 2020).

A nanoemulsion is a colloidal system containing continuous (external phase) and dispersed (internal phase) phases of two immiscible liquids, mainly oil and water. These nonpolar liquids cannot mix, so the nanoscale droplets of one liquid are dispersed into another liquid (e.g., oil in water). The studies reported that oil-in-water (O/W) formulation demonstrated better stability and shelf life. The nanoscale droplet in the formulation provides a high

surface-to-volume ratio that enhances the utility of the formulation. The surfactants or emulsifiers are used as a protective coating material for the oil droplets that prevent creaming and deposition or sedimentation over the period. The hydrophobicity of the surfactants increases the electrostatic repulsive force between the nanodroplets to avoid coalescence. The stability depends on the quantity of the surfactant used in the nanoemulsion (increasing quantity yields more stability). It is important to have a surfactant with both hydrophobic and hydrophilic structural groups for better interaction with water and oil (Bamisaye et al., 2023). A study revealed the nanoemulsion containing palm oil and *Parthenium hysterophorus* L. crude extract (PHCE) for pre-emergence application against slender button (*Diodia ocimifolia*) weed in Malaysian palm oil cultivation. The optimum quantity of *Parthenium hysterophorus* L. extract, palm oil, and surfactants was blended using a high-shear homogenizer. The nanoemulsion showed better weed control with a lesser concentration (5 g L^{-1}) than crude extract alone (10 g L^{-1}). The reason could be better adhesion of the formulation with the plant surface, subsequently increasing the uptake. After 60 days of storage, the nanoemulsion exhibits an increase in particle size (droplets), which can be attributed to the Ostwald ripening phenomena (Zainuddin et al., 2019).

In addition, biopolymers' nano-sized structures act as a shield for herbicide molecules. Hence, biopolymers are biocompatible and biodegradable carrier pesticide materials (Abdollahdokht et al., 2022). The controlled and targeted release of herbicides can be engineered with biodegradable carrier materials such as chitosan (Khan et al., 2023; Li et al., 2023), plant-based NPs (Carvalho et al., 2023; Rodriguez et al., 2022), organoclays (Granetto et al., 2022; Zha et al., 2022), and biodegradable polymers (Schnoor et al., 2018; Mahmoudian et al., 2020; Moore et al., 2022). This review focuses mainly on research related to biodegradable carrier-based herbicides for better weed control while paying more attention to environmental safety. The inevitability of utilizing biodegradable carrier materials in various applications holds significant importance and presents extensive opportunities for developing nanoherbicide formulations. An examination of the crucial role played by sustainable carrier-based nanoherbicide applications in the field of agriculture is provided in this review.

3 Encapsulation of herbicides in biodegradable carrier materials

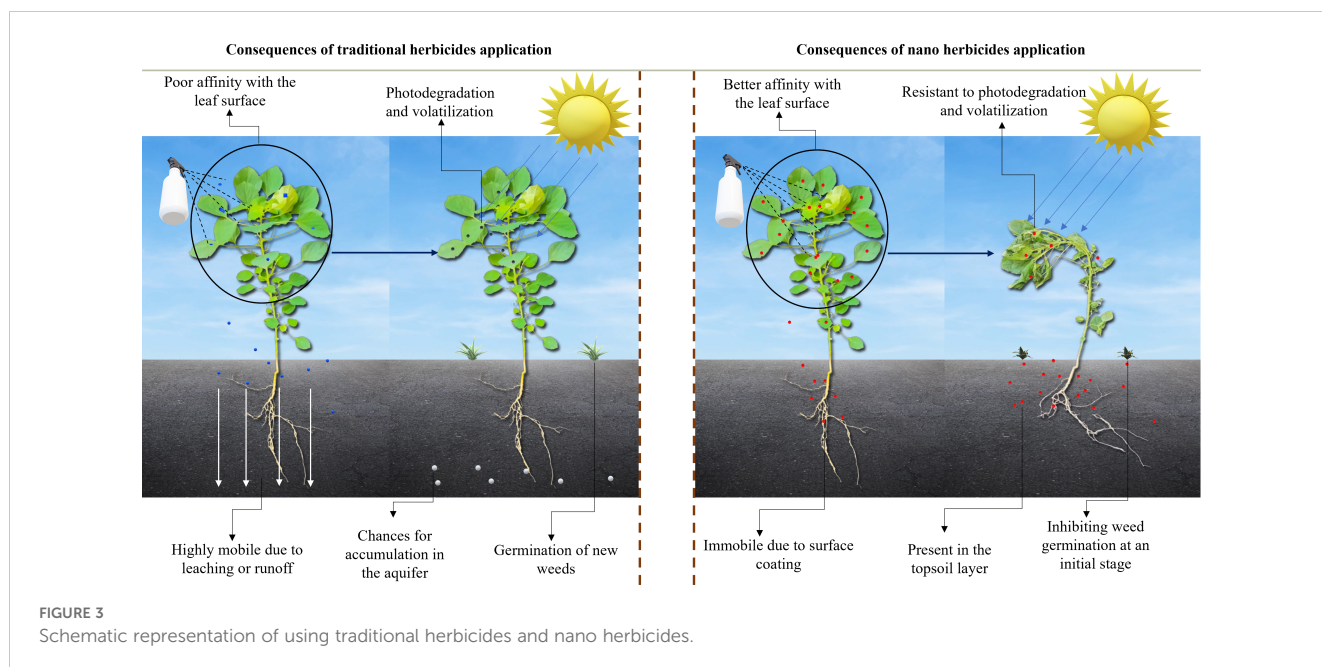
This part of the review highlights the characteristics and compatibility of biodegradable carrier materials. The concept of nanoencapsulation is to reduce the use of high chemical concentrations without compromising efficiency and environmental safety (He et al., 2019). The advantages of encapsulated nanoherbicides include the properties of reduced soil mobility, genotoxicity, and phytotoxicity, which favor the ecological balance (Liu et al., 2021; Bratovic et al., 2023). Nanoscale materials are made of organic and inorganic substances to protect AI molecules. The AIs are protected from

uncontrolled degradations such as hydrolysis, photolysis, volatilization, leaching, and microbial decomposition of agrochemicals. (Nuruzzaman et al., 2016; Xin et al., 2020). Recently, the availability of clay minerals, polymers, metals, and metal oxides has been widely utilized to produce carrier materials to load the active ingredient for the slow-release mechanism (Paul et al., 2024).

The polymer-based nanoencapsulation has been evoked in the interest of longer storage time and easy handling, leading to the prolonged biological viability of the formulation (Chang et al., 2022). In addition, the polymeric nanoparticles exhibit increased efficacy over traditional herbicides by enabling targeted delivery, prolonged release, and better uptake (Machodo et al., 2022). Figure 3 illustrates the difference between conventional herbicides and nanoencapsulated herbicides. The controlled release of nanoherbicides in the plant and soil systems gives environmental compatibility by getting rid of concerns such as runoff and leaching of hazardous substances into the ecosystem (MaChado et al., 2022). Encapsulating AI molecules in carrier materials rather than as being pure active ingredients, increases the herbicidal activity (Forini et al., 2022). For example, essential oil nanoencapsulation showed superior growth suppression capacity and sustained release of herbicidal compounds against the weed species (Campos et al., 2023).

Herbicides that are nanoencapsulated with biodegradable polymers have a biologically active surface that helps better adsorption and penetration in the plant system (Pan et al., 2023). Biopolymers like chitosan, zein, alginates, and synthetic or naturally available polymers can be produced either in the bottom-up or the top-down approach. The top-down approach uses fewer solvents and other toxic chemicals and delivers both hydrophobic and hydrophilic bioactive compounds, easing production at a large scale. The synthesis techniques fall under two categories viz., 1) hydrophobic (emulsion evaporation and nanoprecipitation or solvent displacement), and 2) hydrophilic (ionic gelation and the double emulsion method), and others like photo-crosslinking. The hydrophobic surface of the polymeric nanoparticles is highly preferred for agriculture utilization. The polymeric nanoformulation synthesis technique relies on the type of polymer, AI, and surfactant chosen for the production. For agriculture purposes, nanoprecipitation or emulsion technique is highly preferred. Both techniques methodologically use organic solvents like alcohol, ethyl acetate, and acetone (Shakiba et al., 2020). On the other hand, ionic gelation, double emulsion, and photo-crosslinking methods were often adopted less due to stability and complications in synthesis. Furthermore, Shakiba et al., 2020 have briefly explained each technique. Nanoencapsulation uses different carrier materials to make herbicide formulations. Such formulations have high loading capacity, effective water dispersibility, improved adhesive properties with leaf surface area, and sustained release (Hao et al., 2020). The organoclay minerals represent an alternative selection of carrier materials, offering novel prospects for precise release mechanisms and extended durability within the soil (Paul et al., 2019).

Likewise, the hybrid nanomaterials are an excellent source of carrier materials. It is worthwhile to mention that hybrid NPs are the composites of organoclay-plant NPs (e.g., K10 Na-



montmorillonite/carboxymethyl cellulose) (Granetto et al., 2022), and biopolymer-plant NPs (e.g., chitosan/pectin/sodium tripolyphosphate) (Rashidipour et al., 2019). It also includes combining two different biopolymers (e.g., PLGA/PVA) (Chen and Wang, 2019), and carbon NP-plant NPs (carbon nanotubes (CNT)/gum arabic) (Ke et al., 2021). This combining ability opens up the multidimensional characteristics of NPs and provides an opportunity to develop encapsulated nano-herbicides for sustained release, focused delivery, and escalated affinity on plant parts (Takeshita et al., 2023; MaChado et al., 2022).

The interaction between AI molecules and carrier materials is an important aspect of nano-herbicide production. Van der Waals forces, hydrogen bonding, and hydrophobic interaction drive the affinity between bioactive molecules and carrier materials (Nuruzzaman et al., 2019). The encapsulation of AI molecules using diversified nanomaterials provides control over the release of pesticides, prevents chemical accumulation in the environment, and responds to better weed control (Liu et al., 2021). The AI molecules of plant protectants can be loaded into nanoscale materials. The engineered structures have internal core material (pesticides) and external carrier material (Singh et al., 2023; Wu et al., 2021).

The accelerated or decelerated release of bioactive compounds is believed to be influenced by physical, chemical, and biological degradation, such as hydrolysis, thermolysis, photoresponse, etc (Shakiba et al., 2020). The carrier releases AI on a stimuli-responsive basis, responding to various factors like pH, temperature, enzyme, redox reaction, light intensity, relative humidity, and osmotic pressure (Huang et al., 2018; Camara et al., 2019; Gao et al., 2020; Xin et al., 2020). The overall herbicidal performance of the AIs depends on the release profile of the carrier material.

The dispersion of AIs from the carrier matrix may happen by any release behaviors as follows: Fickian diffusion, swelling or

relaxation, and surface or bulk degradation can cause the initial “burst release” of AIs (Kamaly et al., 2016). In an *in vitro* experiment, pH-responsive release of AI molecules with degradation of carrier NPs at high pH conditions in phloem cells has been confirmed (Xin et al., 2018, 2020). Figure 4 exhibits the available sources of nano-based carrier materials for producing various agricultural nanoscale inputs. The nanoscale carrier materials can be used as a delivery vehicle for beneficial components within plant, human, or animal systems (Patra et al., 2018). The typical smart delivery mechanism of carrier materials, which delivers effective components at site-specific or targeted release in plant systems, is highly appreciable (Liu et al., 2016).

The amphiphilic nature of the carrier materials results in high affinity with the plant surface, thereby increasing the deposition by decreasing the surface tension of the particles (Shangguan et al., 2024). Thus, biodegradable carrier materials are perceived as a reliable source for producing nanoformulations for agricultural systems by anchoring environmental stability. The information suggested that polymeric nanoparticles promise zero toxicity in plant systems and no negative impact on soil microbiota (Shakiba et al., 2020).

In addition, the biopolymer-encapsulated formulations are less soluble, more stable, and non-volatile (An et al., 2022). Compared with the prodrug delivery system in the medical field, the delivery of nano-based agrochemicals is very complex because of their sinking capacity in the ecosystem, which is highly uncontrollable (Shangguan et al., 2024). Hence, this review focuses on the current application and recent development of biodegradable carrier-based nanoherbicide formulations. The encapsulation provides better uptake and enhanced efficacy of agrochemicals against weed control sustainably. The forthcoming section of the review presents the significant discoveries provided in recent research publications related to formulations of biodegradable carrier-based herbicides. The degradable carrier nanomaterials are

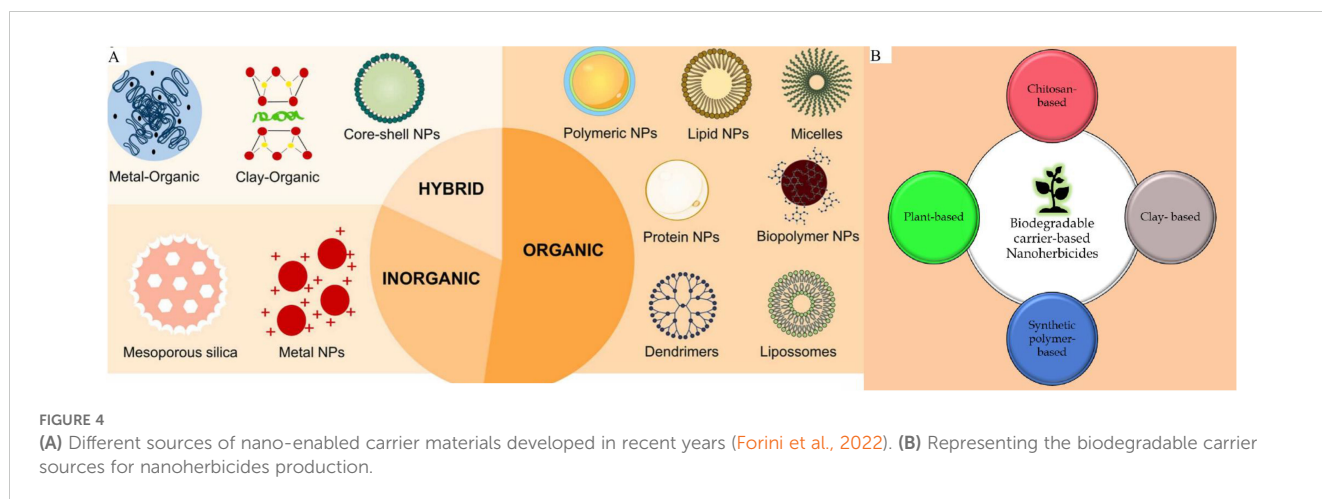


FIGURE 4 (A) Different sources of nano-enabled carrier materials developed in recent years (Forini et al., 2022). (B) Representing the biodegradable carrier sources for nanoherbicides production.

discussed in the sequence viz., 1) chitosan-based, 2) plant-based, 3) clay composite-based, and 4) synthetic polymer-based. Table 1 discusses the key properties, such as source, degradability, thermostability, applicability, and advantages and disadvantages of carrier materials, that have been explored in various studies.

3.1 Chitosan based nanoherbicide

Chitosan is an easily available, widely explored biodegradable, biocompatible carrier material derived from chitin in living organisms. Most of the western and eastern countries have accepted the utilization of chitosan as a nutritional supplement and edible additive in the food industries (MaChado et al., 2022). In addition, chitosan has a variety of applications, including coating fertilizers and seeds, as well as frost protection (Khan et al., 2023).

Chitosan is a naturally available source obtained from chitin deacetylation and has free amino groups, which act as a chelating

agent (Itodo, 2019). Chitosan is a cost-effective and highly permeable NP that can be used for the development of carrier materials for various pesticides, fertilizers, and genetic materials in agriculture (Choudhary et al., 2019; Xin et al., 2020). Additionally, chitosan has the properties of stimulating defense systems and growth promotion in plant administration (Xin et al., 2020).

In a recent study, chitosan-based mesosulfuron methyl and mesosulfuron methyl + florasulam + MCPA isooctyl herbicides were coated successfully. For dose optimization, nanoformulations were applied at the 3-4 leaf stage in a completely randomized block design that includes seven treatments with a pot size of 20 cm x 16.5 cm, and the pot was maintained with 12 weed seedlings. The herbicide formulation sprayed on the weed population based on each treatment. After two weeks, results show 100% weed control recorded in treatment D₂ (nano herbicides at the recommended dose of regular herbicide). In addition, treatment D₃ (5-fold lower dose) was recorded with minimum chlorophyll content (5.57%), plant height (2.35cm), fresh biomass (1.08 g), and dry biomass (0.33 g) (Khan et al., 2023).

TABLE 1 List of biodegradable carrier materials and their key properties.

Properties	Source	Degradability	Thermostability	Application	Advantages	Challenges	Reference
Chitosan	Derivative of chitin present in mushroom, shellfish, etc.,	High	Stable at optimal temperature	Packaging, biomedical and agriculture	Low cost, antibacterial and biocompatible	Prone to brittle in dry conditions and moisture sensitive	(Maliki et al., 2022)
Plant-based	Source from plants viz., starch, cellulose, alginate, etc.,	High	Moderate	Textiles, agricultural composites and packaging	Ecofriendly	Limited thermal stability and hydrophilic	(Zaaba and Jafar, 2020)
Clay composites	Source from clay minerals (e.g., montmorillonite)	Moderate	Comparatively high	Construction, agriculture, and bioremediation	Compatible with other polymers	More degradation time, brittle and processing challenges	(Ali et al., 2024)
Biodegradable synthetic polymer	Derived from fossil fuels (e.g., PCL)	High	Degrades at high temperature	Biomedical, tissue engineering, and drug delivery	Versatile application	Low mechanical strength	(Zaaba and Jafar, 2020; Ali et al., 2024)

In another invitro study, the L-carvone-derived 4-methyl-1,2,4-triazole-thioether complexed with nano chitosan. The L-carvone-derived chitosan derivative has been developed with high drug loading capacity and sustainable release of chemical compounds. The introduction of rigid, bulky, and hydrophobic L-carvone moiety with chitosan improves the compatibility and dispersibility of the 5a compound and enables a multi-stage release mechanism. The compounds have been declared targeted as transketolase (TK)-inhibitors, an enzyme present only in plants involved in the oxidative pentose phosphate pathway and the Calvin cycle. Initially, the compounds 5a-5u were tested in the weed species *Echinochloa crusgulli* L. and *Brassica campestris* at 10 $\mu\text{g mL}^{-1}$ and 100 $\mu\text{g mL}^{-1}$, respectively. Contrastingly, all the compounds (5a-5u) significantly inhibit the growth of dicots (*Brassica campestris*) but are inferior in controlling monocot weeds (*Echinochloa crusgulli* L.). The L-carvone-derived nanochitosan facilitates the adsorption of 5a compounds through its loose and porous microstructure. The release of 5a from the chitosan complex gradually increased after exposure to an aqueous medium, with slow dissolving and disintegration of carriers. The 5a (R = C₆H₅) compound derived from L-carvone-derived 4-methyl-1,2,4-triazole-thioether shows better weed inhibition in the preliminary study than commercial flumioxazin herbicide. The 5a compound was potentially complexed with chitosan compounds such as 7b/5a, 7c/5a, and 7d/5a. The pot experiment revealed that 7b/5a and 7d/5a at the concentration of 100 $\mu\text{g mL}^{-1}$ controlled weed emergence significantly, which is on par with the result of the 5a compound alone. Furthermore, the *Arabidopsis thaliana* transketolase (*At* TK) structure was created by homology modeling and used as a receptor for molecular docking. The Surflex-Dock module of SYBYL X-2.1 has been used to identify the target-site inhibition using molecular docking simulation. Finally, the 5a compound was selected as a representative, and it interacts with receptors and embeds at an active target site of *At* TK, the protein-ligand complex indicates the binding affinity (Li et al., 2023).

Further, Ghaderpoori et al. and Rashidipour et al. prepared different chitosan-based composite nano herbicide formulations in their respective studies, which had paraquat (PQ) AI molecules and tested them on mustard (*Brassica* spp) and corn plants (*Zea mays*). Ghaderpoori et al. revealed that free PQ and chitosan-loaded PQ cause necrosis and fading of leaves in both plants within 48 h. Additionally, the dry weight of corn plants exposed to chitosan composite (sodium tripolyphosphate/xanthan/PQ) was higher than that of free PQ and commercial PQ. In contrast to the corn plants, the mustard plant resulted in less dry weight when exposed to chitosan-loaded PQ over the other two formulations (Ghaderpoori et al., 2020). This implies that encapsulated formulation effectively controls the weed species rather than non-target crops.

Rashidipour et al. reported that composite nano PQ formulation (pectin/chitosan/tripolyphosphate) significantly enhanced herbicidal activity on mustard plants and lower effect on maize plants due to the presence of P-450S glutathione-S-transferase enzyme. The release kinetics was tested in a laboratory condition, where approximately 75% of PQ molecules were discharged after 360 minutes. The nanocomposite formulation

shows reduced cytotoxicity in human lung cells (A549 and KB cells) and mutagenetic effects on *Salmonella typhimurium* and *A. nidulans* (Rashidipour et al., 2019). Some more studies also successfully engaged chitosan NPs and herbicide molecules, which have been furnished for better understanding in Table 2.

3.2 Plant-based nanoherbicide

Plant-based natural polymers such as zein, pectin, and lignin, which are non-toxic and biodegradable, can successfully encapsulate herbicide (Qu et al., 2021). Lignin is an abundantly available biopolymer and is easily converted into humus after decomposition under natural conditions (Rahman et al., 2013). Cyclodextrins are identified as carrier materials for host AI molecules in agriculture. The physiochemical properties, lower cost, easy availability, and nontoxicity to nontarget organisms emanate from its use as a carrier material (Rodríguez et al., 2022; Shangguan et al., 2024).

Carvalho et al. successfully coated Atrazine (ATZ) with Zein NPs (ZNP) and demonstrated a greenhouse study to analyze the pre-emergence herbicidal activity of the synthesized nanoformulation. The experiment was designed based on 7 treatments and 5 replications, which evaluated herbicidal activity, soil retention, and mobility with *B. juncea* as the target and *Zea mays* as the non-target plant. The results revealed that the preemergence application of an 80-fold lesser dose of ZNP-ATZ resulted in 100% mortality in *B. juncea*, as ZNP-ATZ has not shown any mortality or herbicidal activity on nonselective maize plants. In addition, (93.34 \pm 3.42%) free ATZ and (94.02 \pm 1.77%) ZNP-ATZ were retained in the topsoil within 0-4 cm depth. The confocal microscopy results confirmed the accumulation of ZNP-ATZ on *B. juncea* through the root surface rather than leaves (Carvalho et al., 2023). The results reiterate the significance of ZNP-ATZ based on herbicidal activity, selectivity, retention, and accumulation.

Encapsulated essential oil (EO) with polymer matrices acts as a herbicide formulation for controlling weed species (Campos et al., 2023). In a study, red root amaranth (*Amaranthus retroflexus*) and radish (*Rhaphanus sativus*) were treated with starch-encapsulated rosemary essential oil (*Rosmarinus officinalis* L.) as a pre-emergent herbicide under controlled conditions. When the encapsulated formulation was applied at a rate of 5 g/kg soil, it drastically reduced the germination percentages in amaranth and radish by 91.2% and 84%, respectively. In addition, both weeds have been reduced by 51% and 45% in leaf area and by 46% and 54% in root length. Additionally, Alipour et al. (2019) observed a marginal effect of 33% on chlorophyll content in amaranth and 36% in radish.

A similar study covered nano-formulated essential oil (NEO) with naturally available carbohydrate and protein polymers (Arabic gum-gelatin, apple pectin, and gelatin). The application of NEO (3 ml/L) was compared with the traditional chemical metribuzin (1.75 g/L). The results proved that the pre-emergence application of NEO significantly suppressed weed growth under *in vitro* conditions in tomato plant circumstances (Taban et al., 2021). Later, in 2020, Taban et al. further investigated the encapsulation of *Satureja*

TABLE 2 Examples of chitosan-based nanoherbicide formulation and their recent findings for weed control.

S. No	Carrier material	Characterization	Average particle size (nm)	Herbicide molecule	Target weed/Type	Result/Findings	Reference
1	Chitosan	FTIR, SEM, XRD and UV-vis	40-70 nm	Mesosulfuron methyl + florasulam + MCPA isooctyl	<i>Phalaris minor</i> L., <i>Avena fatua</i> L., <i>Chenopodium album</i> L., <i>Lathyrus aphaca</i> L., <i>Angalis arvensis</i> L., and <i>Melilotus indica</i> L.	Various doses of broad-spectrum herbicides significantly influence the chlorophyll content, plant height, fresh biomass, and dry biomass of all the weed species in the wheat crop.	(Khan et al., 2023)
2	Chitosan	UV-vis, FTIR, XRD, SEM, TEM and DLS	-	L-carvone-derived 4-methyl-1,2,4-triazole-thioether	<i>Brassica campestris</i> and <i>Echinochloa crusgalli</i> L.	The complex of L-carvone-derived chitosan carriers enhanced the herbicidal activity.	(Li et al., 2023)
3	Chitosan/Xanthan	SEM and FTIR	-	Paraquat (PQ)	Nontarget- <i>Zea mays</i> Target plant- <i>Brassica spp</i>	Nano-encapsulated PQ herbicide does not have a phytotoxic effect on non-target plants. Expresses stability due to optimal zeta potential, slow release, and better adhesion in plant foliage.	(Ghaderpoori et al., 2020)
4	Pectin, chitosan and sodium tripolyphosphate (PEC/CS/TPP)	HPLC, UV-vis, SEM, AFM, FTIR and DSC	-	Paraquat	Nontarget- <i>Zea mays</i> Target plant- <i>Brassica spp</i>	The herbicidal assay predicts all forms of paraquat growth inhibition in both plants, but <i>Brassica</i> sp. was observed to have more leaf necrosis. The cytotoxicity test in human lung cells and the mutation test on <i>Salmonella typhimurium</i> justifies the eco-friendly trait of nano PEC/CS/TPP-Paraquat.	(Rashidipour et al., 2019)
5	Copper-chitosan (CuCtsNPs)	FTIR, XRD, TEM, UV-vis and EDX	24.68 ± 41.37 nm	Pendimethalin (Pend)	-	Pend-CuCtsNPs were proven to be a good source of slow-release herbicide formulation.	(Itodo et al., 2017)
6	Alginate/chitosan (CS/ALG) and chitosan/tripolyphosphate (CS/TPP)	DLS	400 nm	Imazapic and imazapyr (IMC+IMR)	<i>Bidens pilosa</i> (blackjack)	The encapsulated CS/ALG with IMC +IMR significantly retards the weed growth. It ensures less harm to the soil microbiota and genotoxicity of the <i>Allium cepa</i> plant.	(Maruyama et al., 2016)
7	Chitosan	SEM	60-90 nm	<i>Fusarium oxysporum</i> (metabolites)	<i>Ninidam theenjan</i>	The metabolites obtained from fungi were successfully loaded with chitosan NPs. In addition, the synthesized fungal-based herbicide affects the plant parts and retains phytotoxicity up to 80°C.	(Namasivayam et al., 2015)
8	Glutathione-responsive carboxymethyl chitosan	TEM and DLS	250 nm	Diuron	Target- <i>Echinochloa crusgalli</i>	It was found that disulfide bonding and neutral pH responsiveness are the key factors in herbicide release and stability. The herbicidal performance also reacted well to target and non-target species.	(Yu et al., 2015)

(Continued)

TABLE 2 Continued

S. No	Carrier material	Characterization	Average particle size (nm)	Herbicide molecule	Target weed/Type	Result/Findings	Reference
9	Chitosan/tripolyphosphate	AFM	390-420 nm	Paraquat (PQ)	Model plant- <i>Zea mays</i> and <i>Brassica</i> sp.	The notable benefits of less soil sorption and inhibition on both monocot and dicot plants. The Chinese Hamster Ovary (CHO) cell assay showed reduced cytotoxicity and less chromosomal aberration in <i>Allium cepa</i> .	(Grillo et al., 2014a)
10	PCL/Chitosan	DLS	200-500 nm	Atrazine (ATZ)	-	Chitosan NP successfully coats the PCL-ATZ nanocapsule. The obtained formulation gives high adhesive support to the plant foliage.	(Grillo et al., 2014b)
11	Chitosan	XRD, FTIR, AFM, SEM and UV- vis	40-80 nm	Oregano essential oil (OEO)	-	The chitosan-based carrier formulation resulted in better stability and sustainable release ability.	(Hosseini et al., 2013)

hortensis essential oil (EO) with Persian gum as wall material. The formulation resulted in better stability after 42 days and suppressed *Amaranthus retroflexus* weed growth at the optimized concentration of 15 mL/L of water. Aside from that, the NEO limits the physiological and physiochemical activities (including photosynthesis pigments, phenol, flavonoid, starch, fresh weight, electrolyte leakage, and lipid peroxidation) in the amaranth plant (Taban et al., 2020).

Zein is a naturally available plant protein obtained from *Zea mays* and possesses various properties such as biocompatibility, biodegradability, and hydrophobic surface, which have been highly appreciated for using zein as a biopolymer. For example, Heydari et al. successfully loaded tribenuron-methyl (TM) herbicide molecules in zein nanoparticles (ZNP) and tested their performance against *C. arvensis*, a prevalent broad-leaf weed in the wheat ecosystem. When compared to the commercial formulation of TM, the results confirmed that half of the dose of the TMZNP formulation greatly turns down the percentage of plant height (77%), dry weight (53%), enzyme activity (82%), and acetolactate synthase (ALS) enzyme activity (82%), as compared to the untreated plot (Heydari et al., 2021). Furthermore, many other studies utilize plant-based nanoparticles as carrier materials, and we have tabulated a few such research findings in Table 3.

3.3 Clay composite-based nanoherbicide

Naturally available clays can function as carrier materials for pesticide delivery. Of course, clays can be used to produce commercial nanoherbicide formulations since clays possess ample characteristics (including being eco-friendly, non-toxic, extensively available, and economically feasible). A study reported that montmorillonite-smectite clay minerals can carry herbicide molecules in their layered structure. Smectite clay has the potential for swelling properties, which regulate the release pattern of the herbicide molecules. Montmorillonite-based 2,4-D nanoformulation obtained better desorption and adsorption capacities at low pH under controlled conditions (Paul et al., 2019).

For instance, thermodynamic and kinetic methods modify 2,4-D herbicide with montmorillonite nanoclay. The results provide scope for using 2,4-D modified nanoformulation as a preferable slow-release herbicide against weed growth (Natarelli et al., 2019). Clay modification as organoclay is achieved by replacing inorganic exchangeable cations with organic quaternary ammonium in the interlayers. Consequently, the change in action from a hydrophilic surface to a hydrophobic surface enhances the herbicide loading capacity of AIs between the layered structures of clays (Paul et al., 2019). In addition, clay-polymer composites ensure the controlled release of herbicide molecules while pretending to be an eco-friendly source of carrier material (Nuruzzaman et al., 2019).

Jia et al. reported the loading of glufosinate ammonium (Glu) in the lumen of halloysite nanotubes (HNTs) and incorporated in the biodegradable poly (butylene adipate-co-terephthalate) (PBAT) and Poly (lactic acid) (PLA) mulch films by blow molding and melt blending techniques. The fabricated composite films have been demonstrated in a pot culture experiment with bristleglass as a

TABLE 3 Examples of plant-based nanoherbicide formulation and their recent findings for weed control.

S. No	Carrier material	Characterization	Average particle size (nm)	Herbicide molecule	Target weed/Type	Result/Findings	Reference
1	Zein (Z)	DLS, Zetasizer Nano ZS 90 equipment (Malvern), NTA, AFM, UHPLC, and UV-vis.	130-170 nm	Atrazine (AZT)	<i>Bidens pilosa</i>	It can be used as a post-emergence herbicide in <i>Z. mays</i> . ZNP-ATZ enhanced soil mobility, transport, uptake, and accumulation in <i>B. Pilosa</i> .	(Carvalho et al., 2023)
2	Cyclodextrin (γ -CD)	SEM, EDX, HPLC, and UV-vis	14.1 nm	Disulfide herbicides-aminophenoxazinones (DiS-NH ₂)	<i>Plantago lanceolata</i> , <i>P. oleracea</i> and <i>L. rigidum</i>	Encapsulation of DiS-NH ₂ with γ -CD increases solubility in water and physicochemical properties.	(Rodríguez et al., 2022)
3	Arabic gum-gelatin, apple pectin, and gelatin	SEM, Zeta potential analyzer, and SZ-100 nanoparticle size analyzer	40-77 nm	Savory essential oil (EO)	Amaranth/Pre-emergence herbicide	EO coated with carbohydrate and protein polymers showed better weed control efficiency than commercial Metribuzin.	(Taban et al., 2021)
4	Zein (ZNP)	SEM, DLS and FTIR	120-170 nm	Tribenuron-methyl (TM)	<i>Convolvulus arvensis</i>	Five weeks after the application of herbicides, TMZNP-5 showcased a notable reduction in plant growth and physicochemical activities.	(Heydari et al., 2021)
5	Carbon nanotubes (CNT)/ Gum Arabic	SEM and TEM	-	Glyphosate (Gly)	<i>Arabidopsis thaliana</i>	The synergetic effect of CNT-Gly inhibited the growth of above and below-ground morphology.	(Ke et al., 2021)
6	Magnesium-layered hydroxide/carboxymethyl cellulose (MLH/CMC)	FTIR, XRD, TEM and SEM	219 nm	3-(4-methoxyphenyl) propionic acid (MPP)	-	The layered nanocomposite with CMC improves the thermal stability and pro-long release of MPP and promises environmental safety.	(Hashim et al., 2020)
7	Arabic gum, Persian gum, and Persian gelatin	SEM	<200 nm	Savory oil- <i>Satureja hortensis</i> L. (EO)	<i>Amaranthus retroflexus</i> L.	Nano-EO formulations significantly control weed growth and development. Physiological and biochemical analyses have validated the above results.	(Taban et al., 2020)
8	Starch	UV-vis	-	Rosemary oil (EO)	<i>Amaranthus retroflexus</i>	Pre-emergent application of microencapsulated EO intensively controls weed growth under protected circumstances.	(Alipour et al., 2019)
9	Pectin (polysaccharide)	Particle size analyser, TEM and FTIR	50-90 nm	Metsulfuron methyl	<i>Chenopodium album</i>	The pectin-loaded nanocapsules obtained better control efficacy and reduced competition with wheat crops.	(Kumar et al., 2017)
10	Emulsion (Carvacrol and γ -terpinene)	TEM and DLS	130 nm	(<i>Satureja hortensis</i>) essential oil (EO)	<i>Amaranthus retroflexus</i> and <i>Chenopodium album</i>	Nanoemulsion of EO was examined in both laboratory and field conditions, which control weed growth significantly. The storage of formulations at room temperature doesn't induce phase separation.	(Hazrati et al., 2017)
11	Sodium alginate (ALG)/ CaCl ₂ /Fish scale (ESC)	FTIR, XRD, SEM and UV-vis	-	Diuron and Atrazine	-	The ALG/ESC-CaCl ₂ complex carrier provides steady release and an eco-friendly herbicide formulation.	(Cortes et al., 2017)
12	Solid Lipid	FTIR, UV-vis spectra, DSC, and TEM	111-178 nm	Simazine and Atrazine	Target- <i>Raphanus raphanistrum</i> Nontarget- <i>Zea mays</i>	The pre- and post-emergence applicability of nano-formulated triazine herbicides was confirmed by their slow-release potential and no toxicity to non-target species.	(Oliveira et al., 2015b)
13	Alginate	-	-	Chloridazon and metribuzin	-	Dispersion in water determines the release kinetics of both herbicides and aids in predicting the soil sorption potential.	(Céspedes et al., 2013)

model weed. The overall result shows that PPHG films (PBAT/Poly (lactic acid)/HNT/Glu) significantly controlled the fracture on composite films by up to 51%, reduced water vapor by up to 68%, and reduced the weed incidence by slow release and longer shelf life of the mulch films (Jia et al., 2023).

Garnetto et al. reported that K10-montmorillonite was loaded with commercial dicamba herbicide and coated with carboxymethyl cellulose (CMC), a biodegradable polymer. The K10-CMC-based herbicide formulation was applied to *Solanum nigrum* and *Amaranthus retroflexus* in pot culture under greenhouse conditions. The result concluded that the nanoformulation greatly restricts the volatilization loss and mobility of herbicides in the subsoil. Furthermore, the K10-CMC herbicide formulation obtained lesser biomass on both *S. nigrum* and *A. retroflexus*, with a minimal requirement of 100 g AI/ha and 50 g AI/ha, respectively (Granetto et al., 2022).

In a comparative study, layered double hydroxide (LDH) anionic clay, and Cloisite10A (Clo 10A) cationic organoclay were used as carriers for imazamox (IMZ) herbicide. The herbicide molecules are partially stuffed between the internal layers and stocked on the surface of the clay nanoparticles. Both formulations resulted in a maximum water release of 73 to 98%, after the immediate release of 67 to 93%, which is comparatively lower than the free IMZ (>98%) herbicide release. Additionally, the soil leaching was reduced by 10 to 35% when compared to commercial formulations. The nanoIMZ herbicide molecules are present in the topsoil layer in the range of 5–15 cm, which can be assumed to be a rhizosphere zone. Furthermore, the clay nanoformulation significantly suppressed the growth of the aerial and root systems of *B. nigra* weed species (Khatem et al., 2019). Table 4 displays some recently reported research findings regarding synthetic polymer-based nanoherbicide.

3.4 Synthetic polymer-based nanoherbicide

FDA has approved synthetic polymers like PLGA and PLA for human drug delivery, which indicates their minimal environmental risks (Shakiba et al., 2020). The surface modification of AI molecules with polymer NPs retards the washing off, aggregation, and deposition of NPs, subsequently increasing the uptake and transportation ability of the NPs. The polymeric coating of NPs has better adhesion to the plant surface because of its hydrophobic surface (Su et al., 2019). Moreover, surface-modified NPs exhibited greater penetration potential on the waxy leaf surface (Yang et al., 2015).

Moore et al. reported that PCL-coated nanoatrazine (ATZ) was highly reactive and harmful to human cells. To justify the result, Moore et al. experimented with nano-ATZ, PCL capsules, and ATZ alone in human lung cells (immortalized alveolar type 1-like epithelial cell model: TT1 cells). Nano-ATZ significantly influenced lactate dehydrogenase and cytoplasmic accumulation and co-localized in the Golgi structure, which was confirmed by using a confocal microscope with fluorescent labeling in the

herbicide formulations (Moore et al., 2022). Most studies indicate that applying nano-formulated herbicides may reduce environmental toxicity and increase herbicidal activity. So, moderation in the dosage of nanoformulation is highly desired in agriculture.

De Sousa et al. encapsulated atrazine with PCL NPs, which has been tested as a post-emergence herbicide on *Alternanthera tenella* (Colla plants), at various doses (200, 500, 1000, and 2000 g a.i. ha⁻¹). According to the meta-analysis of previous research findings with the study on *A. tenella*, the nano-ATZ formulation inhibits photosystem II more efficiently than the commercial formulation. In addition, while applying PCL-ATZ, the response of *A. tenella* is different from that of other weed species, where the nano-ATZ obtained more control efficiency than the commercial formulation until 48 hours after the application. The meta-analysis shows that the outcome with *A. tenella* is different from other weed types when it comes to how it responds to nano-ATZ formulation (de Sousa et al., 2022).

In a similar study, Wu et al. compared PCL-coated nanoatrazine with commercial atrazine. They tested both formulations during short-, medium-, and long-term exposure at different concentrations. Lettuce has been a widely used plant for toxicity observation. In this study, the plants were exposed to ATZ and nano-ATZ at nominal concentrations of 0.3, 1.5, and 3 mg per kg of soil. The spectrophotometer readings were observed for all the samples, which indicates the significant influence of nano-ATZ over ATZ in terms of chlorophyll content a and b, carotenoids, hydrogen peroxide production, lipid peroxidation, total protein, and antioxidant enzyme activity. Overall, the ATZ formulation controls the weed growth in the initial phase, but the nano-ATZ shows potential on a long-term basis. Finally, the engagement of both formulations in their respective treatments confirmed nutrient displacement in the soil (Wu et al., 2021).

Takeshita et al. developed an herbicide formulation based on the PCL-metribuzin (MTZ) combination. MTZ can easily accumulate due to the rapid desorption of AI molecules in water. However, the polymer-coated MTZ hasn't shown greater mobility, subsequently lowering the environmental hazards. In addition, the nano-MTZ suppresses *Ipomoea grandifolia* weed species by inhibiting PSII activity with a lower quantity of herbicide formulation (48 g a.i. ha⁻¹) (Takeshita et al., 2022b).

In another study, Schnoor et al. successfully loaded atrazine molecules with poly (lactic-co-glycolic acid) (PLGA). PLGA is a reliable source of polymeric nanoparticles with biodegradable properties, particularly because it will undergo degradation after unloading AIs from the polymer matrix. The AIs were released up to 50% after 72 hours of application in the soil. Furthermore, Schnoor et al. found that the chemical interaction of atrazine and PLGA nanoparticles was justified by the formation of hydrogen bonds at 1.9 Å. The lab study on potato plants with nano-formulation exhibited significant growth retardation in root length, shoot length, fresh weight, dry weight, stem length, and reduced number of leaves (Schnoor et al., 2018). In addition, several synthetic polymer-based herbicide applications and their significance are listed in Table 5.

TABLE 4 Examples of clay-based nanoherbicide formulation and their recent findings for weed control.

S. No	Carrier material	Characterization	Average particle size (nm)	Herbicide molecule	Target weed/Type	Result/Findings	Reference
1	Poly (butylene adipate-co-terephthalate) (PBAT)/halloysite nanotubes (HNTs)	SEM, TEM, EDX, FTIR and XRD	-	Glufosinate-ammonium (Glu)	Green bristle grass	The incorporation of glu-loaded HNTs with PBAT films increased the shelf life of mulch films.	(Jia et al., 2023)
2	K10 Na-montmorillonite/ carboxymethyl cellulose (CMC)	UV-vis	-	Dicamba/systemic	<i>Solanum nigrum</i> and <i>Amaranthus retroflexus</i>	Compared to commercial dicamba herbicide CMC-coated K10 herbicide formulation allows slow volatilization, mobility in soil, and improved weed control.	(Granetto et al., 2022)
3	Attapulgit/Sodium Alginate hydrogels (SAH)	SEM, Zeta potential analyzer, specific surface area analyzer, FTIR, and XPS	500-1000 nm	Glyphosate (Gly)	-	SAH-Gly encapsulation sustains the release of Gly molecules in the soil.	(Zha et al., 2022)
4	Attapulgit/Calcium alginate (ATP/CA)	FTIR and XRD	-	Glyphosate (Gly)	<i>Vallisneria spiralis</i>	ATP-Gly-CA was exposed to an electrical field in crop weed <i>in vitro</i> conditions. It increases the release of Gly from the composite formulation at different volts. In addition, the composite formulation assures biosecurity concerns and suppresses weed growth.	(Zhang et al., 2020)
5	Magnesium-aluminium (MgAl-LDH)/sepiolite fibrous clay/ Alginate- Zein (A-Z)	XRD, FTIR, NMR and SEM	0.77-2.15 nm	2-methyl-4-chlorophenoxyacetic acid (MCPA)	-	The construction of nano-MgAl-LDH/Sep composites and A-Z polymeric protection unveils the sustainable release of MCPA herbicides in water.	(Rebitski et al., 2019)
6	Cloisite 10A (Clo10A)/layered double hydroxide (LDH)	XRD, FTIR, SEM and HPLC	225-306 nm	Imazamox (IMZ)	<i>Brassica nigra</i>	The results of biodegradable Imz-LDH and Imz-Clo10A resemble the same characteristics in release profile, herbicide toxicity, and environmental compatibility. Both composites show better efficacy when compared to conventional IMZ.	(Khatem et al., 2019)
7	Hexadecyltrimethylammonium-saturated Arizona montmorillonite (SA-HDTMA)/calcined hydrotalcite (HT500)	HPLC	-	R-Imazaquin	<i>Brassica oleracea botrytis</i>	The SA-HDTMA organoclay and R-Imazaquin complexes provide significant adsorption capacity, slow degradation, and release in the topsoil. Root growth inhibition by herbicide formulation affects the aerial growth of the weed flora.	(López-Cabeza et al., 2019)
8	Montmorillonite nano clay	XRD and FTIR	-	2,4-Dichlorophenoxyacetic acid (2,4-D)	-	The process of exfoliation in montmorillonite clay absorbed 2,4-D herbicide. The release mechanism has been described as a burst release followed by a constant, slow release.	(Natarelli et al., 2019)

(Continued)

TABLE 4 Continued

S. No	Carrier material	Characterization	Average particle size (nm)	Herbicide molecule	Target weed/Type	Result/Findings	Reference
9	Na ⁺ -montmorillonite derived pillared clay Fe/(Fe+Al)/cyclodextrin (CD)	SEM and FTIR	-	Picloram (PCM, 4-amino-3,5,6-trichloro pyridine-2-carboxylic acid)	-	The release kinetics and solubility of complex PCM-(Fe+Al) clay-CD in sand soil flattened release compared to the traditional formulation.	(Marco-Brown et al., 2017)
10	Montmorillonite (MMT)/clinoptilolite (CL)-Sodium Alginate (Alg)	FTIR, SEM, XRD and UV-vis spectra	-	Paraquat (PQ)	-	As per the examined results, intercalated MMT/PQ showed controlled release compared to CL/PQ. Furthermore, the encapsulation of PQ, clay, and Alg provides the scope for flattened release.	(Rashidzadeh et al., 2017)
11	Kaolinite	FTIR, DSC, TEM, XRD and UV-vis	-	Amitrole (AMT)/(3-amino-1,2,4-triazole)	-	Methoxy-modified KaoH functions as an efficient carrier of AMT and enhances the slow-release of nanoformulation.	(Tan et al., 2015b)
12	Starch gel-Montmorillonite (MMT)	XRD, SEM, and FTIR	230 nm	Ametryne	-	Starch gel and MMT clay successfully implemented the dual coating principle, resulting in the gradual release of AI molecules.	(Giroto et al., 2014)
13	Fe-pillared clay mineral (Fe PILCs)-cyclodextrin (CD)	XRD	-	Imazaquin	-	In the comparative study of Al and Fe-PILC, the Fe complex of PILC, along with CD provides, enhanced herbicidal properties.	(Undabeytia et al., 2013)
14	Tubular halloysite (Hal)/platy kaolinite (Kaol)	UV-vis, XRD, TEM, and CHNOS elemental analyzer	239 nm	Amitrole (AMT)	-	Methoxy-modified Hal has the high-loading capacity of AMT. On the other hand, methoxy-modified Kaol provides a slower release of AMT compared to Hal.	(Tan et al., 2015a)
15	Halloysite nanotubes (HNTs)-PVA/starch composites (ST)	FTIR, TEM, SEM, XRD, UV-vis, and Zwich/Roell instrument	5-50 nm	Atrazine (ATZ)	-	A dual delivery system of carrier materials, viz., nonencapsulated herbicide and nano-intervened mulch film, enhances the persistence and biological effect of ATZ molecules in the soil.	(Zhong et al., 2017)

TABLE 5 Examples of synthetic polymer-based nanoherbicide formulation and their recent findings for weed control.

S. No	Carrier material	Characterization	Average particle size (nm)	Herbicide molecule	Target weed/Type	Result/Findings	Reference
1	PCL	DLS and AFM	>450 nm	Atrazine (ATZ)	-	NC-ATZ is more toxic to humans when compared to ATZ alone. However, it has weed-control properties and reduced environmental toxicity.	(Moore et al., 2022)
2	PCL	-	243 ± 5 nm	Atrazine (ATZ)	<i>Alternanthera tenella</i>	NanoATZ showed better inhibition capacity for PSII activity compared to commercial ATZ.	(de Sousa et al., 2022)
3	PCL	DLS and AFM	289 ± 3 nm	Metribuzin (MTZ)	-	PLC-encapsulated nanoMTZ provides better sorption and slower desorption in organic matter-rich soil profiles.	(Takeshita et al., 2022b)
4	PCL	DLS and AFM	289 ± 3 nm	Metribuzin (MTZ)	<i>Ipomoea grandifolia</i>	With increased weed control, NanoMTZ resulted in lower aquifer contamination because of lower retention and mobility in the soil.	(Takeshita et al., 2022a)
5	PAA HCL/ polystyrene sulfonate	-	-	Sulfentrazone, oxyfluorfen, diclosulam, and metolachlor	-	Encapsulated diclosulam recorded the minimum weed density, weed dry weight, higher productivity, and profitability of groundnut yield.	(Swetha et al., 2022)
6	PCL	SEM	>100 nm	Atrazine (ATZ)	Model plant- <i>Lactuca sativa</i>	In comparison of nanoATZ and commercial ATZ, nanoATZ claims its greater influence on plant growth, photosynthesis, ROS production, stress-related enzyme activity, and elemental uptake.	(Wu et al., 2021)
7	PEG	-	-	Sulfentrazone (Sulf)	Grasses, sedges, and broad-leaved weeds in irrigated Groundnut.	Pre-sowing application of encapsulated nanoSulf ensures better weed control and increases crop yield significantly.	(Srimathi et al., 2021)
8	PCL	SEM	120 ± 10 nm	Atrazine (ATZ)	Model plant- <i>Lactuca sativa</i>	The nanoATZ have longer persistence and slow-release potential in the soil significantly influencing the metabolism and growth of non-target microbial colonies.	(Zhai et al., 2020)
9	PCL	-	-	Atrazine (ATZ)	<i>Digitaria insularis</i> (sour grass)	Compared to regular ATZ, the nano-ATZ was well-acted as a photosystem II inhibitor on <i>D. insularis</i> . Subsequently, it decreases the initial growth of the weed so that nano-ATZ can be used as a post-emergence herbicide in maize culture.	(Sousa et al., 2020)
10	PMMA	FTIR, SEM, TEM and UV-vis	100-300 nm	Haloxypop-R-methyl	-	The results confirmed the steady release of polymer-encapsulated herbicide and Trito-X100 as the best surfactant for nanoformulation	(Mahmoudian et al., 2020)
11	PCL	DLS and NTA	256-345 nm	Atrazine (ATZ)	Model plant- <i>Brassica juncea</i>	PCL encapsulation ensures the slow release of ATZ, as well as increased AI accumulation within the cell organelles. It also confirmed PCL's biodegradability and biocompatibility.	(Bombo et al., 2019)

(Continued)

TABLE 5 Continued

S. No	Carrier material	Characterization	Average particle size (nm)	Herbicide molecule	Target weed/Type	Result/Findings	Reference
12	PCL	FTIR, AFM, and TEM	150-250 nm	Metribuzin (MTZ)	Target- <i>Portulaca oleraceae</i> (Purslane) Nontarget- <i>Glycine max</i> Gene test- <i>Allium cepa</i>	The PCL encapsulation influences greater stability, and release ability in target and nontarget species. NanoMTZ exhibits better inhibition of <i>Portulaca oleraceae</i> growth, without affecting the growth of the <i>Glycine max</i> plant.	(Diyanat and Saedian, 2019)
13	PCL	FTIR, AFM and TEM	70-200 nm	Pretilachlor	Target- <i>Echinochloa crusgalli</i> (Barnyard grass) Nontarget-Paddy	Nano-formulated pretilachlor significantly suppresses weed growth and is compatible with the paddy ecosystem. The gene alteration test shows that nanoherbicide causes fewer toxicity effects on <i>Allium cepa</i> genes.	(Diyanat et al., 2019)
14	PCL	-	260 nm	Atrazine (ATZ)	<i>Amaranthus viridis</i> (slender amaranth) and <i>Bidens pilosa</i> (hairy beggarticks),	The application nanoATZ greatly reduces root and shoot growth in both weeds over the commercial atrazine formulation.	(Sousa et al., 2018)
15	PLGA/PVA	DLS and SEM	204-520 nm	Atrazine (ATZ)	-	Adding PVA to the PLGA-ATZ leads to greater emulsion stability and controlled release.	(Chen and Wang, 2019)
16	PMMA	TEM, SEM, and FTIR	60-100 nm	Haloxypop-R-methyl	<i>Lemna minor</i> L.	Encapsulated herbicides at different doses significantly influenced the photosynthesis and enzymatic activity of the target weeds.	(Torbati et al., 2018)
17	PLGA	DLS, TEM, and FTIR	110 ± 10 nm	Atrazine (ATZ)	Potato plant	The results proved that polymer-coated AI is an environmentally sustainable source of weed control. Degradation of the PLGA matrix doesn't produce any toxic substances.	(Schnoor et al., 2018)
18	PEG	DLS	1-100 nm	Pretilachlor	<i>Echinochloa crusgalli</i>	Pre-emergence application of microemulsion (ME) and monolithic dispersive (MD) forms of pretilachlor significantly suppresses weed growth in paddy crops. Especially ME provides better results when compared with MD and commercial formulations in most of the weed control parameters.	(Kumar et al., 2016)
19	Perylene-3-yl methanol (Pe)	FTIR, TEM, and UV-vis	25 nm	2,4 dichloro phenoxy acetic acid (2,4-D)	<i>Cicer arietinum</i>	The adsorption of Pe-2,4-D nanoherbicide into plant tissue was facilitated by the size of herbicide molecules, resulting in growth inhibition.	(Atta et al., 2015)
20	PCL	-	-	Atrazine	Nontarget- <i>Zea mays</i>	ATZ-loaded PCL polymer proved to be the safest method of weed control in maize crop, supported by its detoxifying ability.	(Oliveira et al., 2015b)
21	PCL	NTA	240.7 nm	Atrazine	Model plant- <i>Brassica juncea</i> (Mustard plant)	Compared to commercial ATZ, post-harvest application of nanoformulation decreases photoreactions and infuses senescence in plant parts.	(Oliveira et al., 2015a)

(Continued)

TABLE 5 Continued

S. No	Carrier material	Characterization	Average particle size (nm)	Herbicide molecule	Target weed/Type	Result/Findings	Reference
22	PCL	-	408.5–483.1 nm	Atrazine (ATZ)	Target- <i>Brassica</i> sp. Nontarget- <i>Zea mays</i> Model plant- <i>Allium cepa</i>	NanoATZ proved to have the properties of target inhibition, longer availability in soil, and minimal genetic alterations.	(Pereira et al., 2014)
23	PCL	AFM and TEM	293 ± 5 nm	Atrazine	-	Slow release has been achieved after the relaxation of the polymer coating, with an initial rapid release followed by a controlled release.	(Kah et al., 2014)
24	PCL	FTIR, AFM, and TEM	232–290 nm	Atrazine, Ametryn and Simazine	-	Encapsulated nano-triazine herbicides retained their stability after 9 months, and their test on human white blood cells and <i>Allium cepa</i> proves the formulation is eco-friendly.	(Grillo et al., 2012)

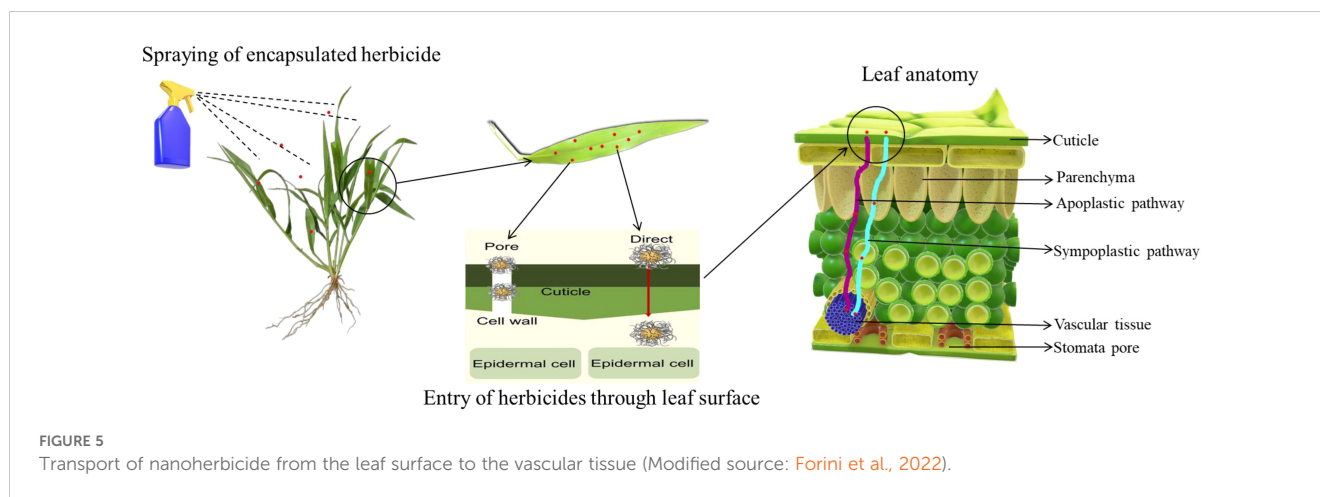
4 Uptake, transportation, and fate of nanoherbicide in plant systems

Research publications have reported fewer experimental results regarding nanoparticle absorption, mobility, and cellular-level modifications in the plant system. Furthermore, the extent of uptake and mobility of NPs have been determined by the plant canopy conditions and the properties of NPs, including size, shape, and charge, along with the morphology of the plant (Singh et al., 2023). The vascular structure transports the NPs to other parts after they penetrate a specific area through the leaf or root surface (Judy et al., 2012; Lead et al., 2018). Figure 5 illustrates the movement of herbicide molecules from the leaf surface to the vascular tissue.

According to Rajput et al. (2020) and Tripathi et al. (2017), nanoparticles can be translocated from root to aerial parts through xylem (soil application) and aerial parts to root through phloem (foliar application). The foliar application showed better uptake efficiency than the soil application in the plant system. The uptake of NPs in plants takes place in three steps, viz., 1) deposition of NP on the surface of the root, leaf, or stem, 2) NP penetration via epidermis and cuticle, and 3) NP translocation within the plant system. Plant species have similar phenotypical features in their leaves, with distinguished arrangements in an epidermis having stomata, mesophyll, and vascular tissue based on the environmental habitat and plant species' evolution over the years. In addition, the cuticular pathway acts as a secondary barrier, which is resistant to allowing any particle larger than 5 nm (Su et al., 2019; Ali et al., 2021).

Stomatal opening size ranges on the micrometer scale, which is another way for the NPs to penetrate the leaf surface; it occupies more than 5% of the total leaf surface area. But the opening of stomata differs in each plant in response to external factors like carbon dioxide concentration, RH, light intensity, and temperature (Su et al., 2019). Minuscule unenclosed parts in the plant leaf such as stomata, hydathodes, cuticles, and trichomes, facilitate the entry of NPs into the plant cell (Singh et al., 2023). On the other hand, dissolved NPs in water can reach the root indirectly by capillary movement and enter the root tissue through osmotic pressure (Chen, 2018). The roots are another mode of entry for NPs inside the plant system, where a higher root surface area results in better uptake potential for NPs. In addition, the root system's micromorphology consists of an endodermis, pericycle, cortex (solid and lacunate), and vascular bundle in the center. However, the solid cortex and endodermal casparian strips make it hard for NPs to move through the apoplastic because of their compacted intercellular spaces (Su et al., 2019).

It is worth mentioning that variations in the structural morphology of leaves and roots determine the penetration and restriction of NPs. The NPs can enter the xylem vessels through the symplastic or apoplastic pathway and then accumulate in the cellular and subcellular organelles (Tripathi et al., 2017) through trailing transportation (root tissues, endocytosis, protein carrier, plasmodesmata, or through pore formation) (Pérez-de-Luque, 2017). Once NPs reach the xylem, the upward movement of NPs takes place, whereas the downward movement of NPs takes place through the phloem cells, respectively (Su et al., 2019). Extremely



small-sized NPs can penetrate the cell organelles or membranes of plants and be absorbed directly with their diffusive capability (Xin et al., 2020).

The effects of nanoherbicides on lipid peroxidation, chlorophyll content, protein content (Pontes et al., 2021; Wu et al., 2021; Oliveira-Pinto et al., 2022), electrolyte leakage, chromosomal aberration (Diyant et al., 2019), reactive oxygen species (ROS) production (Pontes et al., 2021), carbon dioxide assimilation rate (Takeshita et al., 2021), and photosystem I and II yields (Pontes et al., 2021) have been investigated (Forini et al., 2022). The lipid envelope exchange penetration (LEEP) property of chitosan NPs eases penetration into the cell organelles through the nanoscale size and surface charge of the NPs (MaChado et al., 2022). It is emphasized that the hydrophobic-hydrophobic interaction of nonpolar molecules found on plant surfaces and composite nanoformulation promotes the effective adhesion of nanopesticides in plant foliage (Hao et al., 2020; Forini et al., 2022).

The soil application of NPs translocates the AI molecules to other parts of the plant with the help of vascular tissues (MaChado et al., 2022). The secretion of negatively charged substances from the root surface, such as mucus or organic acids resulted in the absorption of positively charged chemical inputs (NPs) from the soil (Lv et al., 2019). The intracellular movement, or protoplast pathway, is the primary movement of NPs and is influenced by plasmodesmata, which have a diameter of 2-20 nm (Kaphle et al., 2018). To remove the barriers to understanding the mobility and uptake of nano-pesticides, labeling of polymeric NPs with fluorescent markers would act as a tracker system for the indication of the translocation pathway (Proença et al., 2022; Shakiba et al., 2020; Takeshita et al., 2023).

The permeability of bioactive NPs into plant cell walls has not been characterized, it also depends on the size and hydrophobicity of the NP (Avellan et al., 2019). NPs with amphiphilic properties and about 40 nm in size can move through cells more easily than NPs that are hydrophilic and large-sized (Santana et al., 2020). To confirm the translocation ability and targeted delivery of NPs in plant organelles, hydrophilic quantum dots (QD) coated with amphiphilic β -cyclodextrin NPs were used to facilitate translocation through leaf cell wall pores. The modified QDs are

injected into the *Arabidopsis thaliana* leaf in 3-4 weeks, successfully delivered by peptide-guided targeted delivery at chloroplast cells. The fluorescence intensity of QDs in chloroplast cells was imaged through confocal microscopy (Santana et al., 2020). Once again, the fluorescent labeling of NPs shows successful tracking of uptake and translocation pathways, which is supported by the results of foliar-applied PCL NPs (Bombo et al., 2019) and root-applied Zein NPs (Prasad et al., 2017). Isothiocyanate and rhodamine are widely used fluorescent probes for nano-constructed polymeric NPs (Proença et al., 2022). The poly(ϵ -caprolactone) (PCL) nanocapsules containing atrazine (ATZ) herbicide successfully coated with chitosan (CS) polymer. The PCL/CS+ATZ nanoformulation inhibits the PSII system, and the relative electron transport rate significantly controls the growth of the *Bidens pilosa* plant. Additionally, the endogenous atrazine quantity at the plant tissues' leaves, stems, and roots was estimated using Carvalho et al.'s methodology with slight changes (Carvalho et al., 2023). The PCL/CS+ATZ and commercial ATZ quantity on plant tissues fluctuated according to the exposure duration viz., 2, 4, 8, 12, 24, 36, 48, and 72 hours. The root contains the same amount of free ATZ and PCL/CS+ATZ after 72 hours @ $17 \pm 2 \mu\text{g/g}$ of root tissue. Whereas PCL/CS+ATZ recorded the highest quantity after 24 hours @ $14 \pm 2 \mu\text{g/g}$ of stem tissue, it was comparatively lesser than free ATZ quantity. The leaf tissues are recorded as having the highest accumulation of both formulations compared to the quantity of stem and root tissues. After 72 hours, leaf tissues contain $25 \pm 2 \mu\text{g/g}$ of ATZ released from PCL/CS+ATZ formulation (Sousa et al., 2024).

5 Future perspective and development

To balance the food crisis in the context of the burgeoning population, climate fluctuation, water shortage, and reduction in arable land, the need for cutting-edge technology is urgent to ensure global food security (Xin et al., 2020). The use of NPs in agriculture is inevitable, although it has several advantages and disadvantages. It was anticipated that NPs could reduce production-improving chemicals that pose a severe risk to human health and the soil-plant

system (Rajput et al., 2020). The nanoencapsulated herbicides are a good choice for achieving sustainable agriculture, reducing the dependence on conventional herbicides and toxicity. The properties of traditional pesticides would have to be masked by synthesizing polymeric nanoformulations with enhanced colloidal stability and lesser polydispersity, along with successful entrapping or encapsulating of biologically active chemical compounds (Shakiba et al., 2020). However, the disintegration of AI molecules from polymer matrix has been observed in certain instances. The nano-encapsulation with organic polymers has encountered difficulties, including formulation instability and the formation of acid monomers due to polymer degradation (Abdollahdokht et al., 2022). Thus, the nanoformulation should be highly stable 1) until it reaches destiny (target inhibition), 2) as compared to commercial formulations, and 3) without compromising environmental safety.

Conventional pesticide formulations are mixtures of inert substances like alcohol, ketones, and benzenes with active chemical compounds. Due to their extreme toxicity and potential for severe poisoning, all of these substances are dipolar solvents and highly hazardous to human health (Paul et al., 2024). To address this concern, nanoencapsulated biodegradable herbicide formulations should be produced as a much-needed priority. The producers need to pay attention to the selection of polymers and surfactants available with a high surface charge that creates a high electrostatic repulsive force among the particles, which can be confirmed by the zeta potential value (higher or lower than 30 and -30 mV) (Hans and Lowman, 2002; Shakiba et al., 2020). For instance, Zwitterionic surfactants are less hazardous and an excellent choice for environmentally friendly surfactants since they possess cationic and anionic characteristics (Paul et al., 2024). Integrating Zwitterionic surfactants may also enhance the formulation stability, yielding a longer shelf life.

Surface-engineered biodegradable NPs may change their surface potential and electrostatic interaction due to the adhesion of NPs inside the plant system. We can clearly understand that the stability of NPs inside plant systems highly depends on the solute composition of the plant system (Rodrigues et al., 2017). It may result in the aggregation of NPs, which causes poor transportation of NPs in the plant system. The importance of surface coatings is receiving more attention, and further efforts are needed to produce a stable wall matrix until it reaches the target site.

A survey of recent articles on nano-encapsulated biodegradable herbicides shows that the size of NPs ranges more than 100-1000 nm. The plant uptake of NPs is well documented; it indicates superior translocation occurred when the particles are at 1-100 nm nanoscale. Nano-sized particles are known for better uptake and transportation in the plant system. So, future studies on nanomaterials should focus more on particle sizes that fall under the nanoscale range.

Few studies have been reported on the nanoencapsulation of essential oils (EO), but impressive results were provided in controlling weeds. The encapsulation has improved herbicidal capabilities with an improvement in viability, persistence, and targeted delivery against weed species (Campos et al., 2023). Essential oils are derivatives of plant materials, providing an

option for producing bioactive herbicides. Encapsulating EO with carrier material is a better strategy to widen the production of EO-based herbicide formulations. However, nanotechnology has been considered a novel technology in various fields. Nevertheless, risk assessment methods must be developed for future endeavors relying on nanotechnology. Thus, future research must be conducted on understudied materials to produce readily biodegradable and non-toxic products.

Few studies have investigated the quantification and translocation of herbicide molecules in plant anatomy. Therefore, more focus should be placed on framing the quantification methodology to estimate the accumulation of bioactive compounds in plant tissues. However, injudicious usage of nano-herbicides also causes lethal environmental and human hazards. The researchers have to focus on dose optimization and the persistence of herbicide molecules. The cohort study on the organisms involved could assist in gaining more knowledge on the fate and effect of NPs.

Even though herbicide encapsulation shows enormous benefits, slow release is the top priority. In weed control, timely germination inhibition and growth restriction must be done without fail; otherwise, crop-weed competition will lead to yield loss. The encapsulated formulation may limit the release of AIs from the core-shell matrix at the critical weed growth period. Likewise, instead of solving one problem, we should not create another problem by encapsulation or loading the bioactive compounds. The studies experimented with the release kinetics were based on the invitro conditions, where factors like RH, temperature, moisture, and solar radiation are uncontrollable in field conditions. So, the nano-encapsulated herbicides must be trailed under different environmental conditions, which can direct optimization of the formulation according to adverse conditions.

6 Conclusion

The current trends in agriculture are heading towards sustainable agriculture. "Green herbicides" with zero toxicity are highly desirable in modern agriculture. In this context, the research community highly recommends nano-enabled biodegradable herbicides to ensure global food security. Furthermore, the study highlights the significance of nano herbicide application for weed control. This review will convey the benefits and limitations of nanoencapsulated herbicide application. Consequently, we have formulated the immediate need for attention to nanoherbicide application. The unfathomable benefits of using nano-herbicides enhance the interest in unveiling the new horizons of nanotechnology. The studies have to focus on the mode of action of herbicide formulations. The studies should consider the following suggestions: 1) commercial production is obsolete because of the need for open field trails rather than laboratory or controlled conditions; 2) studies on risk assessment and tracking of NPs were subjected to a lower-than-anticipated count; 3) selection of compatible carrier materials; 4) focusing more on different crop ecosystem to analyze nontarget effects. Lawmakers, research communities, and manufacturing industries should focus more on

the abovementioned limitations. This review will bring clarity and confidence about toxic-free herbicide production and application in the agricultural ecosystem. In addition, the focal point of this review is the biodegradable carrier-based nanoherbicides, which gives insights to researchers, manufacturers, and students on how to take this topic to further advancement.

Author contributions

RJ: Conceptualization, Investigation, Methodology, Resources, Writing – original draft, Writing – review & editing. PR: Conceptualization, Investigation, Resources, Supervision, Validation, Writing – review & editing.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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