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Review

Mof-enabled pesticides as developing approach for sustainable agriculture and reducing environmental hazards

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ABSTRACT

In the context of agricultural sustainability and the necessity for food security, using nano pesticides as an innovative technology represents an alternative with good potential to overcome the drawbacks of classical pesticides. This work provides a general overview of the main aspects in the area of nano-pesticides with a focus on Metal-Organic Frameworks (MOFs). Although in its early infancy, the research performed so far indicated that compared with classical pesticides, MOF-based nano-pesticides show an improved performance, controlled and sustained active ingredient release and targeted delivery. Moreover, the flexibility in design and capability for modification and hybridization indicate MOFs as promising candidates for further improvements. Nevertheless, since the long-term toxic effects of MOF-based nano-pesticides are not yet fully understood, additional studies focusing on the impact of individual components and of the overall nano-system are required to determine if the envisioned potential can be reached.

Contents

Abbreviations: AIs, Active ingredients; Alg, Alginate; BET, Brunauer-Emmett-Teller; BPY, 4,4′-bipyridine; CMC, Carboxymethyl Cellulose; CMCs, Carboxymethyl Chitosan; CMS, Carboxymethyl Starch; Cs, Chitosan; CTD, Clothianidin; Da, 2,4-dinitrobenzaldehyde; DCS, Differential scanning calorimetry; DLS, Dynamic light scattering; DNA, Deoxyribonucleic acid; EBNB, (E)-di (p-3-nitrobenzoic acid) ethylene; EDTA, Ethylenediaminetetraacetic acid; EFSA, European Food Safety Authority; FAO, Food and Agriculture Organization of the United Nations; GSH, Glutathione; HKUST, Hong Kong University of Science and Technology; KSM, Kasugamycin; MIL, Materials Institute Lavoisier; MOF, Metal-Organic Frameworks; MTT, 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2H-tetrazolium bromide; NMOFs, Nano-MOFs; NPs, Nanoparticles; NTA, Nanoparticle Tracking Analysis; P, Pectin; PMMA, Polymethylmethacrylate; PNIPAm, Poly (N-isopropyl acrylamide); PYR, Pyraclostrobin; SLNs, Solid lipid nanoparticles; TA, Tannic acid; TMX, Thiamethoxam; UiO, University of Oslo; ZIF, Zeolitic imidazolate frameworks; γ-CD, γ-Cyclodextrin.

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Introduction

Pesticides are chemicals used to defend against pests and plant diseases and to promote agricultural production growth [1–5]. Their most common active ingredients include organophosphates, carbamates, chlorinated hydrocarbons, and carbamide derivatives. Based on statistics from the Food and Agriculture Organization of the United Nations (FAO), pesticide control of pests and pathogens has restored 30% of the total output of agricultural products worldwide [6,7]. Nevertheless, global pesticide usage increased to 4.1 million tons per year in 2017, of which 90% was released into the environment, redistributed in the ecological cycle during the application or remained in crops [8,9]. Improper pesticide usage severely threatens the environment and human health, leading to problems such as resistance to pathogens and pests, bioaccumulation in the food chain, soil degradation, eutrophication of water, and dissipation of biodiversity. Pesticide exposure can occur through inhalation, dermal contact, breathing, and dietary intake [10,11].

Conventional pesticides have a variety of disadvantages, such as poor dispersibility, a large amount of organic solvent, dust drift, and the ability to remain in the soil for a long time. Water-insolubility is another limitation of pesticides, which should be processed into a suitable formulation by solvent, carrier, dispersant, emulsifier, or other auxiliary materials for simplifying the spray in the field [12]. The two main formulations of traditional pesticides are wettable powder and emulsifiable concentrate. The wettable powder is a powdered pesticide formulation consisting of active ingredients (AIs) of pesticides, inert fillers, and other materials. The inorganic fillers of wettable powder are easily transferred to the environment. However, the loaded AIs in wettable powder cannot be released entirely and residual pesticides are degraded with difficulty. The emulsifiable concentrate is a liquid formulation of pesticides. A stable emulsion is a mixture of AIs dissolved in the organic solvent and emulsifier diluted with water. During pesticide spraying, organic solvents and toxic substances directly leak into the environment, producing serious contaminants in the soil and water system and resulting in chemical residues in products and food materials [13,14].

Due to the widespread usage of pesticides, the main challenges of pest resistance, environmental contamination, bioaccumulation, and toxicity require urgent intervention. One possible option is the reduction of the number and quantity of pesticides used. In this regard, nanotechnology has been recognized as an enabling tool that offers new solutions for the formulation and delivery of active ingredients of pesticides [15]. Nano size, high surface area, and target-modified characteristics of nanoparticles (NPs) are significant parameters in applying nanomaterials in pesticide formulation [16]. As a result, nano formulation-based products have advantages compared to conventional products, including

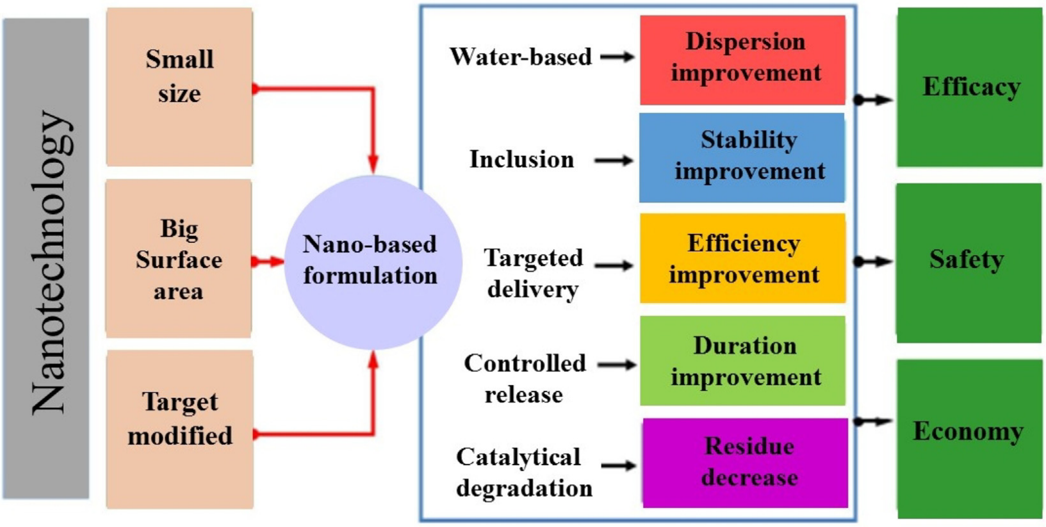

Fig. 1. Advantages of formulation based on nanotechnology.

improved formulation properties (permeability, stability, and dispersion of the active ingredients), reduction of applied doses, more efficacy, easy application, enhanced environmental safety, extended effective duration, and better delivery to the target [17] (Fig. 1).

Nano formulation pesticides are developed based on two groups, nanoparticles directly applied as pesticides and pesticides loaded in nano carriers. Various nanomaterials are used to manufacture nano pesticides, including metal and non-metal oxides, carbon-based materials, quantum dots, polymers, lipids, and metal–organic frameworks (MOF) [18,19]. Because of the significance and attractiveness of nano-pesticides, numerous studies and reviews have been performed [14,15,20–22]. Nano formulations can have significant effects on the fate of active ingredients and may introduce new ingredients with poorly understood environmental fate, such as nanosilver [21]. In 2014, Kookana et al. [22] discusses potential modifications to existing assessment tests and procedures to accommodate nano pesticides, covering areas such as analysis and characterization, environmental fate and exposure assessment, ecotoxicity, and risk assessment in aquatic and terrestrial ecosystems. The primary focus is on determining whether the presence of nanomaterials in pesticide formulations introduces any significant differences compared to conventional active ingredients. In 2017, a book chapter was written about nano pesticides [14], which initially addressed the necessity of using pesticides and highlighted the limitations of conventional insecticides. It then introduced nano pesticides, discussing their advantages and disadvantages, as well as describing various types of nanomaterial-based insecticides. Finally, it mentioned that due to the emerging nature of these nanomaterials and the lack of sufficient toxicity assessments, the consequences of their use are still uncertain and require further investigation. In a review paper published in 2021 [15], Chaud et al. covered the sources of nano pesticides, the negative environmental and health effects resulting from pesticide exposure, and the potential benefits of nanoparticles in improving agricultural productivity and addressing ecosystem challenges. They explored strategies for controlled release and stimuli-responsive systems for delivering pesticides and genetic material in a slow, sustained, and targeted manner. They addressed concerns and issues related to the development, formulation, and toxicity of pesticide products. Then in the middle of 2021, Shekhar and colleagues [20] evaluated the consumption patterns of nano pesticides and their potential health impacts. They aimed to bridge the gap between the need for effective pest control, environmental sustainability, associated benefits, and the potential harmful effects of nanoagrochemicals.

Like other fields such as energy production and storage, sensors, pharmaceuticals and drug delivery, adsorptive removal of pollutants [23–26], in recent years MOFs have received significant attention in the development of nano pesticides, and products with suitable efficiency have been developed. Given the growing application of these compounds in the field of nano pesticides, the current focus is mainly on the development of MOF-based nano pesticides. In this context, this review briefly overviews different types of nano pesticides, their features, benefits, risk assessments and discusses, focusing primarily on the MOF-based nano pesticides.

Nano pesticides: features, properties, and benefits

Nano-pesticides can be categorized into (i) pesticides with nano-sized active ingredients, which usually include a nano-dispersant emulsion of active pesticides, and (ii) pesticides loaded, encapsulated, doped, or coated by nanomaterials [27,28]. The central concept behind pesticide nano formulation is to increase deliv-

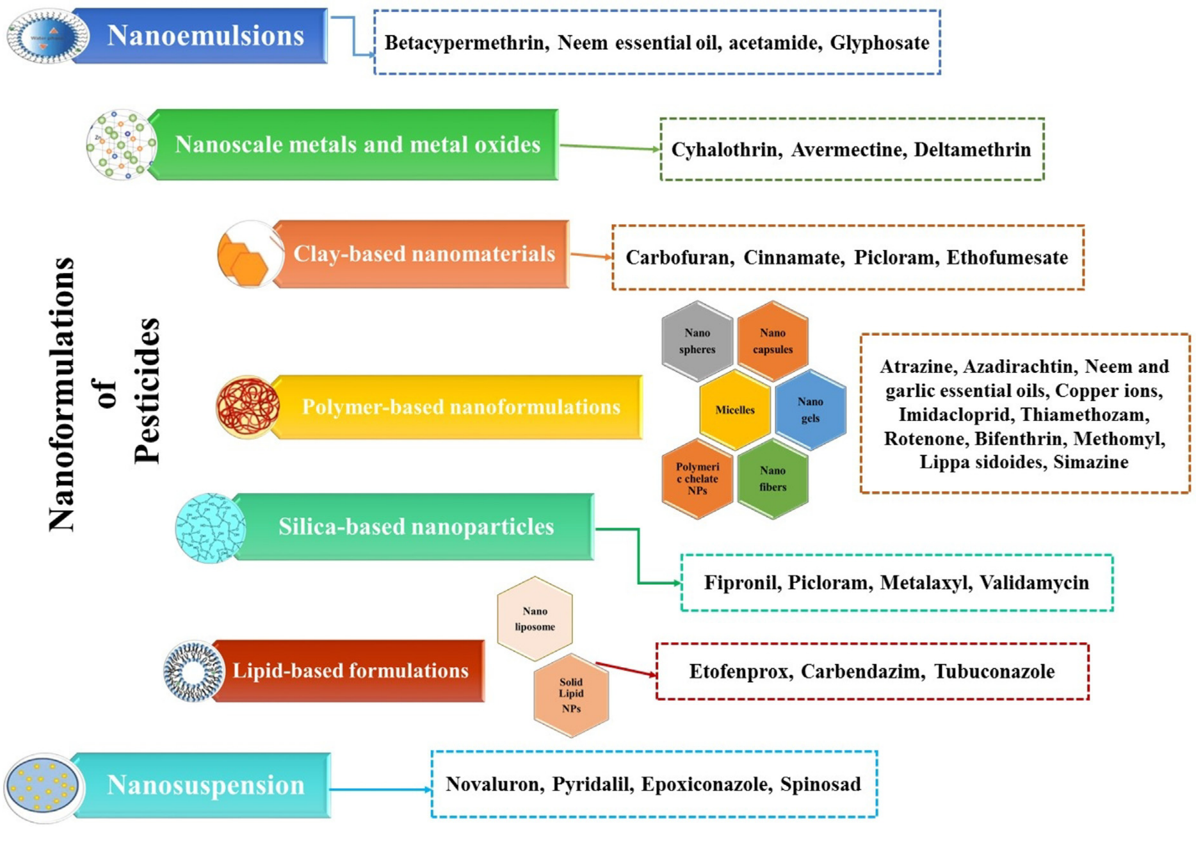

Fig. 2. Various type of developed nanoformulation-based pesticides.

ery and efficacy. They offer a wide range of advantages, including (i) reducing the release rate of active ingredients, (ii) improving the solubility of the active ingredients, and (iii) achieving targeted delivery and improving chemical stability [18,22]. Various nano formulation types have been developed, including nano-emulsions, polymer-based formulations, nano suspension, nanoscale metals and metal oxides, lipid-based formulations, clay-based nanomaterials, and silica-based nanoparticles [21,29], Fig. 2.

The ***nano-emulsions*** are generally developed to improve the solubility of poorly water-soluble active ingredients and to increase the spreadability and mechanical stability. Moreover, they have good bio-availability and chemical stability. Nano-emulsions can be categorized into two major groups. (i) thermodynamically stable (have a potent repellent surfactant at concentrations above the critical micelle concentration and are used for nonpolar pesticides that are somewhat soluble in water). (ii) kinetically stable (are formed when the pesticides are insoluble in the aqueous phase, and the aggregation of the surfactant into the micelles is low due to poor repellent surfactant) [30–32].

Due to the minimal use of organic solvents and surfactants, ***polymer-based nano formulations*** permit a slow and controlled release of active ingredients, provide protection against degradation, and enhance the performance of active ingredients while reducing adverse effects on the ecosystem. The polymers used in nano pesticides primarily include polysaccharides (such as chitosan, alginates, and starch) and polyesters (such as polyethylene glycol and poly-ε-caprolactone).

Nano suspensions are nano dispersions of active ingredients as solid nanoparticles in an aqueous medium stabilized by surfactants. The surfactants are arranged on the nanoparticle surface, the polar portions extend into the aqueous media, and the nonpolar parts are bonded on solid nano pesticides. The significant advantages of nano suspensions are enhanced chemical stability, improved bioavailability, and controlled release mechanisms [21,33].

Metal and metal oxide NPs. The metal and metal oxide NPs have a series of advantages, including a high surface-to-volume ratio, high thermal stability, flexibility of the pore size, significant pore volumes, and effective surface properties [34]. In addition, they have biocidal activity through 3 primary mechanisms: (i) destroying molecular microorganisms structures by releasing superoxide radicals during photocatalysis; (ii) rupturing the cell membrane by accumulating metal nanoparticles; (iii) impairing DNA replication via uptake of metallic ions into cells. These nanoparticles can be used alone as active ingredients or with conventional pesticides in the nano formulation [35,36]. Different metal NPs can be considered for various uses. For example, silver (Ag) NPs have strong antifungal, anti-bactericidal and antiviral activity [37,38]. TiO_2 has antimicrobial and antifungal effects, with a high potential to reduce the ecological and toxicological effects on non-target organisms [39,40]. Copper (Cu) NPs can damage bacterial wall cells, and pesticide formulations based on them are cheaper and more efficient than conventional biocides [41,42]. Zinc oxide (ZnO) NPs are inexpensive and have low toxicity [43]. The size range of ZnO NPs can influence phytotoxic effects, including effects on the physiological level and the cell level [44]. Aluminum (Al) NPs can protect stored products from pests [45], and studies show that they are more effective than toxic diatomaceous earth formulations [46]. Porous silica NPs have good biocompatibility, porosity, higher loading capacity and efficient delivery. Compared to polymeric nanoformulation, they are structurally flexible and mechanically more stable. Silica nanoparticles enhance plant tolerance to biotic and abiotic stresses, and variants charged hydrophobic surfaces were applied to control pests and to decrease fungal infections [47,48].

The ***lipid-based nano pesticide formulations*** have a decrease in chemical degradation, a combination of hydrophobic and hydrophilic active ingredients, the possibility of large-scale commercial production, and prevention of the photo-degradation of active ingredients [49,50].

MOFs, also called coordination polymers, are porous crystalline materials whose structures have formed from metal ions and organic linkers. In recent years, MOFs have received considerable attention in the delivery system due to advantageous properties, including high specific surface area, high porosity, stability, adjustable pore size and well-ordered pores. Also, they show excellent loading efficiency and slow-release performance [51,52]. For example, an nano carrier for avermectin (AVM) delivery was prepared utilizing Cu-based MOF constructed of 1,3,5-benzenetricarboxylate (BTC) [51]. The Cu-BTC enhanced the cytotoxicity and contact toxicity of AVM by 42.4% and 39.6% compared to free AVM. It slowly released at least 91.5 % of loaded AVM during 120 h while prevented pesticide degradation. Regardless of formulation type, it is anticipated that these nano-pesticides can mitigate the most significant drawbacks of conventional pesticides, increase their efficacy, enhance the stability of active ingredients, and lengthen the duration of effectiveness. Table 1 shows various formulations with applications of the resulting nano-pesticides.

Advantages

Less than 0.1% of applied pesticides reach their intended targets, whereas more than 99.9% enter the environment, causing soil, air, and water pollution [99]. Insoluble or poor solubility in water is one of the disadvantages of many pesticides. Large quantities of organic solvents are needed to overcome it, which enhances the cost and leads to additional environmental contamination [13]. Also, the excessive and nonselective usage of traditional pesticides affects the ecosystem balance and human health. It leads to main problems such as increasing resistance to pathogens and pests, decreased soil biodiversity, elimination of beneficial soil microbes, and destruction of pollinators and beneficial natural enemy species [100].

In this context, nanotechnology is an alternative, offering a platform for targeted delivery and controlled release of pesticides by preparing nano-sized active ingredients or nanomaterials-based agrochemical formulations [101]. Decreasing the size to the nanoscale has advantages such as (i) reduction of non-target effects, durability enhancement, minimization of active ingredients used, and diminution of residues and pollution [102]; (ii) by reducing the active compounds, the cost of production declines and the bioavailability and permeability improve; (iii) the water solubility of insoluble or poorly soluble active ingredients is improved. In addition, it improves droplet adhesion and increases effectiveness against pests [15,32,103].

The dispersion of hydrophobic active ingredients is increased in aqueous solutions by polymeric matrix nano-encapsulation, which allows a controlled release with high selectivity and without obstructing biocide activity. It prevents early degradation, extends the longevity of pesticides and improves the formulation stability [104,105]. Nanocapsulation technology can reduce the amount of pesticides applied, eliminate the offensive odors of the released chemicals, stabilize unstable core materials, and decrease degradation and evaporation [29]. The nano-microcapsule formulations also show protective performance and slow release because polymer materials utilized to prepare them are light-sensitive, humidity-sensitive, soil pH-sensitive, and thermo-sensitive [106]. Fig. 3 presents a general view of the main advantages of nano-pesticides.

Table 1
Different types of pesticide nano formulations and their features.

Nanoformulations	Active ingredients	Attributes	Ref.
Nanoemulsions			
Tween 80 and lecithin	Pyrethrum	Improved activity	[53]
Tween 80 and glycerol	Piper belle or betel leaf essential oil	Improved activity	[54]
Palm kernel oil ester	Parthenium hysterophorus crude extract	Herbicidal activity	[55]
Gelatin-chitosan, Tween 20, Span 60	Cinnamaldehyde and α-tocopherol and garlic oil	Antimicrobial and antioxidant	[56]
Alkyd resin	λ-cyhalothrin	Increased water stability	[57]
Calcium dodecylbenzene sulfonate and NP-6	Bifenthrin	Increased stability	[58]
Emulsifier	Pyriproxyfe	Improved activity and lower toxicity	[59]
Tween 80	Chlorpyrifos-methyl, diazinon, and malathion	Increased activity and stability	[60]
Span 85, Brij 97, ethylene glycol	Citral	Increased stability and extended activity	[61]
Glycerol, Tween 80, Agnique BL1754	Tebuconazole	Improved stability	[62]
Tween 80	Pimpinella anisum essential oil	Improved stability and efficiency	[63]
Polymer (nanoencapsulation)			
Poly(lactic-co-glycolic acid)	Imidacloprid	Enhanced effectivity with reduced dose	[64]
Polyethylene glycol	Clofentezine	Improved persistence and solubility	[65]
Poly(ethylene glycol)	Diethylphenylacetamide	Enhanced effectivity	[66]
Polylactic Acid	Permethrin	Enhanced the persistence	[67]
Poly(ε-caprolactone) and chitosan	Atrazine, ametryn, simazine	Increased stability, controlled release	[68]
polymer poly lactic acid, poly (lactic-co-glycolic) acid	Propiconazole	Enhanced effectivity	[69]
Polymer (Nanospheres)			
Poly(ε-caprolactone)	Azadirachtin	Reduced UV-degradation	[70]
Gelatin and methyl methacrylate	Tebuconazole	Decreased leaching losses	[71]
Poly(vinyl alcohol) and glyphosate	Glyphosate	Temperature responsive controlled release	[72]
Poly(lactic-co-glycolic acid)	Pyraclostrobin	Enhanced release	[73]
Polymer (Nanogels)			
β-cyclodextrin	Permethrin	Reduced biodegradation	[74]
Poly(vinyl alcohol)-valine	Emamectin benzoate	Long duration of pest control	[75]
Polyethylene glycol and 4,4-methylenediphenyl diisocyanate	λ-cyhalothrine		[76]
Pectin, chitosan, sodium tripolyphosphate	Paraquat	Enhanced activity	[77]
NanoSuspension			
Emulsifier 700	Lambda-cyhalothrin	Decreased amount of surfactant	[78]
Polyvinylpyrrolidone	Chrysanthemum coronarium, Azadirachta	Antibacterial activity	[79]
Sodium alginate, Tween 80	Pyridalyl	Increased toxicity	[80]
Polycarboxylate, MRES, sucrose	Abamectin	Improved bioavailability	[81]
Isobutyl acetate, isopropanol, surfactants	Novaluron	Increased efficiency	[82]
Metal and metal oxide NPs			
Ag NPs	Cyhalothrin	Enhanced delivery efficiency	[83]
Ag NPs	-	Larvicidal and pupicidal activity	[84]
Ag NPs	Profenofos	Increased efficiency and activity	[85]
Ag NPs	–	Fungicidal and biological activity	[86]
Cu NPs	–	Antibacterial activity	[87]
Cu NPs	–	Insecticidal activity	[88]
CuO NPs	–	Antifungal property	[89]
TiO_2 NPs	–	Antibacterial activity	[39]
Ag doped hollow TiO_2NPs	–	Enhanced fungicidal activity	[90]
TiO_2 NPs	–	Increased efficiency	[91]
Al_2O_3 NPs	–	Insecticidal activity	[92]
ZnO NPs	Thiram	Antifungal activity	[93]
Mesoporous silica NPs	2,4-D sodium	Increase of pesticide loading	[94]
Mesoporous silica NPs	Chlorantraniliprole	Enhanced loading of pesticide	[95]
Lipid-based nanoformulations			
Beeswax, coil, Tween-80	Deltamethrin	Reduced photodegradation	[49]
Dimyristoylphosphatidylcholine, Tween 20, dimyristoylphosphoglycerol	Trifluralin	Improved performance	[96]
Nanoliposomes	Eucalyptus citriodora oil	Stimuli-responsive release	[97]
Liposomes	Etofenprox	Controlled release	[98]

Physicochemical properties

Understanding the physicochemical properties of nano pesticides enables determining their mode of action and the optimal selection of the best-suited variant in a given circumstance. Particle size, chemical composition, dissolution, stability, and agglomeration/aggregation level vary significantly depending on the chemical nature and formulation [107].

The ecotoxicity of conventional pesticides is usually associated with active ingredient mass concentration. For nano-pesticides, other factors could be essential to determine the bioavailability and toxicity, such as nanoparticle concentration, size distribution and the free and nanoparticle-bounded active ingredient ratio [22]. For example, it was observed that smaller-sized particles show more saturated solubility and dissolution [108]. The mean particle size and width of particle size distribution can determine physicochemical features like dissolution velocity, physical stability, saturation solubility, and biological performance. Analytical approaches for determining particle size distribution and concentration include DLS as a scattering technique, NTA as a particle

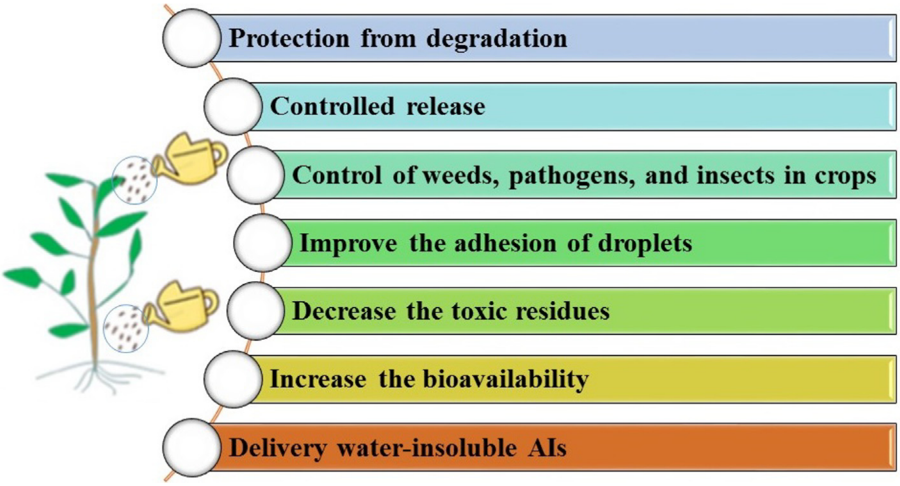

Fig. 3. The main advantages of nano pesticides.

tracking method, centrifugal methods like DCS, and fractionation. The degree of dispersion or agglomeration of nano pesticides changes over time and depends on concentration and environmental parameters like ionic strength, pH, and dissolved molecules in the media [22]. Consequently, it is crucial to characterize nano pesticides at different periods of their environmental life cycle.

The octanol/water partition coefficient (K_{ow}) is a significant parameter in predicting the affinity for lipid-rich tissues of non-target organisms. However, K_{ow} is determined with difficulty because they do not partition into either phase. Instead, they accumulate at the interface of the ethanol/water due to their high surface energy [109]. Pesticides have concentration-independent dissipation, absorption, and distribution, whereas nano formulations are concentration-dependent. Phase partitioning depends on nano particles' agglomeration status, size, and surface charge [22].

Used as a pesticide or carrier material, nanomaterials have demonstrated advantageous properties, such as crystallinity, stiffness, thermal stability, permeability, and biodegradability. The high surface area is correlated with a high surface free energy, which aids the flocculation of nanoparticles. Flocculation and aggregation of nanoparticles can decrease the effectiveness of active ingredients and enhance bioaccumulation and toxicity. So, most nanocarriers and nanoparticles have a stabilizing agent on the surface to improve the zeta potential and, or control steric effects to promote the repulsion of nanoparticles [110,111].

Fate of nano pesticides in the environment

Similar to conventional pesticides, nano pesticides can affect the biochemical or photochemical phases of photosynthesis and ecosystems. Therefore, their behavior and fate are crucial factors during and after usage. Unfortunately, studies on the ecotoxicological impacts of nano pesticides are scarce, especially considering their fate and environmental behavior.

The fate models of conventional and nano pesticides are expected to differ. These differences arise from the active ingredients release from nano pesticide complex, phase partitioning, agglomeration and changes in the distribution of nanoparticles size and degradation, as well as concentration dependence of all the above parameters. The nano nature changes the environmental fate of active ingredients, such as degradation, sorption, volatilization, and persistence. In this regard, the following scenarios are possible:

(i) The pesticide fate related to nano formulation depends on the durability of the nano-pesticide. Durability is a criterion that indicates the time a nanocarrier pesticide preserves its integrity after use. The durability of nanocarrier pesticides can be classified into three groups, (a) rapid release of active ingredients (the nano formulation is solely used as a delivery mechanism for pesticides' active components, and it is anticipated that the nanoformulation's behavior will not differ from that of pure active chemicals); (b) slow release of active ingredients (due to the incomplete destruction of encapsulated pesticides or the binding of active chemicals to other components, the release of active substances from nanocarriers is either very slow or incomplete); (c) no dissolution of active ingredients (the release of active ingredients is not possible due to the nano pesticide resistance to degradation).

(ii) By controlling nano formulation properties, the apparent dispersion/solubility of the active ingredients is enhanced, or the degradation is changed. For example, enhancing the active ingredients' solubility cause increased mobility and quicker degradation by soil microorganisms. Another possibility is that surfactants affect the sorption of active ingredients, depending on the type and concentration of the surfactant. The biotransformation of nanomaterials in the environment can also significantly influence their environmental fate and persistence due to their interaction with biological organisms and plants.

The nanoparticle characteristics can be changed by the dynamic interaction of nanomaterials with the surrounding environment and the absorption/adsorption of numerous moieties on its surfaces [112–115].

Several available fate and transport models can currently model organic chemicals in different environmental areas, like the FOCUS models such as PRZM, PELMO, MACRO, PEARL, and TOXSWA. In addition to critical criteria explored for conventional pesticides that presumably play a crucial role in differentiating their fate, additional particle-related factors must be considered for nano pesticides. Furthermore, studies have elucidated that the majority of physiochemical and environmental factors affecting the nanomaterials´ fate are common among the different types of materials, for instance: i) for aqueous media: salinity, pH, ionic strength, microorganisms, and dissolved (and suspended) organic matter; ii) for soil media: soil type, pH, porosity, temperature, water flow, mineral composition, microbial consortium, amount and type of natural organic matter, especially humic acids, and electrolytes (particularly divalent cations).

Some nano formulations have limited stability; upon contact with soil solution, aggregation or agglomeration is likely to occur. For instance, the presence of ions in the environment affects the agglomeration behavior of nanoparticles, and the behavior of a nanomaterial in freshwater and saltwater is distinct. Dilution can also influence the fate of various active ingredients. The cases mentioned above may also apply to conventional pesticides. The only nano effect may be associated with nano-dispersion, where faster degradation and weaker adsorption are anticipated. Additional experiments must be conducted under realistic conditions to determine whether these effects will significantly affect the distribution, transport, and degradation. The environmental fate of some nano formulations is summarized in Table 2.

Risk assessment and toxicity of nano pesticides

Risk assessment

Due to the possibility of deposition and accumulation of pesticide residues with lipophilic properties, the distribution of pesticides in ecosystems affects not only the intended organisms but also the entire living world. Before introducing a new pesticide product, precise safety tests must be performed to avoid undesirable risks it exerts. It is anticipated that these risks may be mitigated by nano pesticides by reducing exposure levels. The increased bioavailability and/or bioactivity of nanomaterial-based AIs compared to bulk material rises the health risk, and there is the possibility of altering their mechanism of action. Furthermore, carriers/co-formulates used in nano formulation can be bioactive and dangerous.

Risk assessment comprises exposure appraisal, peril evaluation and characterization, and risk determination [128]. There can be different ways for humans to be exposed to pesticides; for example, occupational exposure for workers using pesticides and non-occupational usage of pesticides originating from food, drinking water, or air containing residual traces. In these cases, skin contact, inhalation, and ingestion exposure can occur [10,129].

The current paradigm of health danger evaluation applied for chemicals (with a few exceptions) could be modified to assess the risk possibility of nano-pesticides. However, additional data and testing methods are required. When dealing with nano pesticides, extra requirements for toxicity tests include i) the AIs degradation; ii) the degradation of the nanocarrier or nanoparticle; and ii) the degradation or dissociation of the nanocarrier-AIs complex. The transformation processes of the AIs, nanocarrier, nanoparticle, and nanocarrier-AI complex (like dissolution, hydrolysis, etc.) must also be considered when distinguishing exposure and evaluating toxicity, particularly in a post-application. According to the European Food Safety Authority’s (EFSA) guide for nanomaterials risk evaluation in the feed and food chain, all co-formulants/auxiliary materials (such as solvents, surfactants, and carriers) used in the formulation of nano pesticides must be performed. Even if the safety of all AIs or co-formulants has been independently confirmed, the safety of all constituents must be evaluated.

As with conventional pesticides, the environmental risk assessment of nano pesticides requires data and information regarding the physicochemical properties and nano formulation of AIs, behavior and fate in various environmental segments, determined or estimated ecological concentrations, and ecotoxicity for relevant species. Since the physicochemical properties of nanomaterials significantly impact their interactions with biological tissues, their toxicity kinetics, pharmacology and potential toxicity can also be affected. The risk of a pesticide to human health can be reduced or increased by nano formulation (e.g., nano formulations or nano-size AIs can often decrease the amount of AIs required, reducing exposure). All living organisms in the environment are impacted by pesticides or pollutants deposited in the soil, and it was shown that $Cu(OH)_2$-based nano pesticides can alter soil microbiota, interfering with the breakdown of the neonicotinoid thiacloprid [130].

Toxicity

The toxicology studies identify and characterize in vivo hazards of nano pesticides through in vitro and in silico evaluation methods. Toxicokinetic studies (including the absorption, distribution, metabolism, and excretion), acute systemic toxicity, short-term and long-term toxicity, skin and eye irritation, genotoxicity, reproductive and developmental toxicity and carcinogenicity are required for all AIs [131].

Toxicity towards the target species and organisms is one of the essential characteristics of pesticides. Toxicity results from inhibitory and stabilizing agents and organic solvents are used to avoid the attachment of undesirable colloids. The rapid progress in nano pesticides development has raised concerns about the possibility of their bioaccumulation and subsequent introduction into the food chain. The toxic effects of pesticides and nano compounds on living creatures are not sufficiently assessed, especially considering the many pesticides used and their possible interactions.

Studies show that the quantity reaching a particular target can be enhanced due to the variation in the AI’s penetration through biological impediments [132]. For example, the release and bioavailability study of bifenthrin as a nano-encapsulated pesticide for two earthworms (Eisenia fetida and Lumbricus terrestris) showed that nano formulations remained in the worm’s guts but were eliminated well than the classical bifenthrin [133]. Atrazine and simazine loaded into solid lipid nanoparticles (SLNs) have a slow release and high stability. Their cytotoxicity in fibroblast cells was low as measured by the MTT assay (20% less than the commercial variants). SLNs did not affect the growth of the non-target organism (*Zea mays*), but they were ten times more effective than common herbicides at killing *Raphanus raphanistrum* [134]. The

Table 2
Environmental fate of some nano formulations.

Nano formulation	Feature	Pesticide	Ref.
Nanoemulsion	Reduce hydrolysis	Triazophos	[116]
Nanoemulsion	Increase solubility and prolong the release	Beta-cypermethrin	[117]
Nanosphere and nanocapsule	Slow release	Atrazine	[118]
Polymer nanocarrier	Increase sorption without degradation change	Atrazine	[119]
Polymer nanocarrier	Slow release and degradation	Bifenthrin	[120]
Polymer and lipid nanocarriers	Slow release and decrease degradation	Chlorpyrifos and Tebuconazole	[121]
Polymer nanocarrier	Rapid release and short durability	Clothianidin	[122]
Porous hollow silica NPs	Slower degradation due to UV-shielding	Avermectin	[123]
Solid lipid NPs	Lower evaporation	Artemisia arborescens L essential oil	[124]
Nanoparticles	Faster degradation	Imidacloprid	[125]
Nanoparticles	Slow release	Paraquat	[126]
Polymer nanocarrier	Controlled release	Imidacloprid	[127]

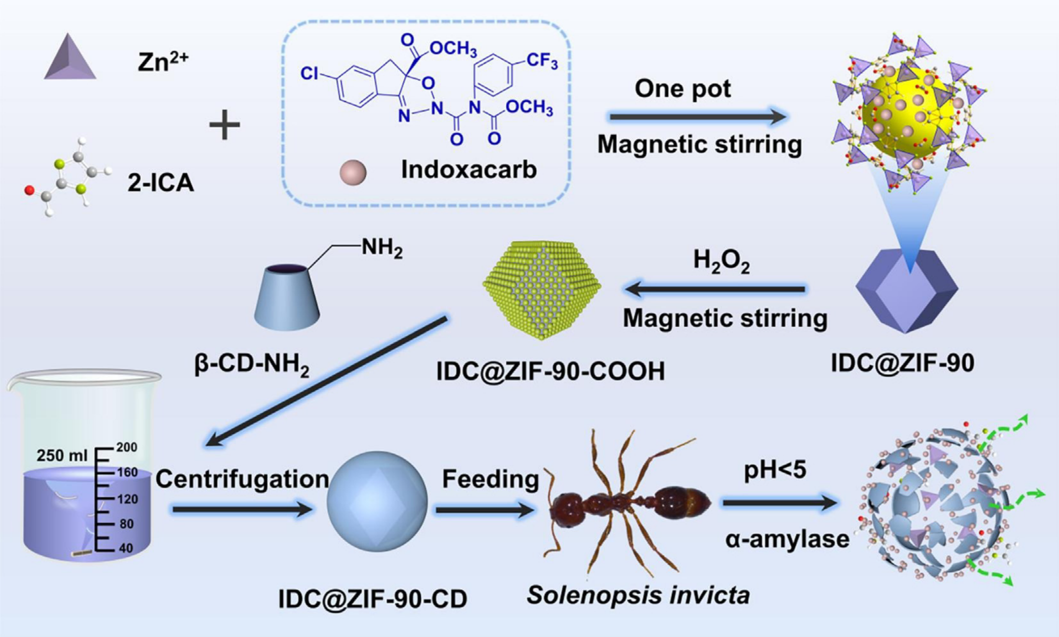

Fig. 4.T. He synthesis procedure for production of idc@zif-90-cd and its smart pesticide activity against red imported fire ants. Adopted with permission from [136].

in vivo toxicity of unloaded SLNs affected the survival and body length of *C. elegans* nematodes. Because the effects of loaded and unloaded NPs were similar, it can be concluded that the increased toxicity is due to the specific SLN formulation and not the insecticide alone [135]. Yang et al. [136] utilized the β-cyclodextrin modified with an amine-contacting organic moiety of mono-(6-amino-6-deoxy), abbreviated as β-CD-NH_2, to develop a delivery system based on intelligent pH and α-amylase dual triggered-responsive pesticide. They integrated ZIF-90 and β-CD-NH_2 and loaded the product with indoxacarb Fig. 4.). The fabricated nano formulation with about 249 nm particle size provided 18.4% loading efficiency. β-cyclodextrin-functionalized MOF enhanced toxicity towards the red imported fire ants, and it was shown that zeolitic imidazole skeleton-90 (ZIF-90) has a high potential in efficient pesticide

Table 3
MOF-based nano pesticides used in agriculture.

MOF-enabled pesticides	Loaded pesticides	Specification/ or stimuli	Role	Ref.
C_3Cl_2@MOF-1201, C_3Cl_2@MOF-1203	cis-1,3-dichloropropene	Crop nutrition	Fumigant	[150]
*Tebuc@PCN-224@P@C	Tebuconazole	Dual-microbicidal	Fungicide	[156]
PYR@FeMOF-pectin	Pyraclostrobin	Dual stimuli-responsive	Fungicide	[157]
CAP@NH_2-MIL-101(Fe)-CMS	Chlorantraniliprole	Triple stimuli-responsive, crop nutrition	Insecticide	[153]
CAP@MIL-101(Fe)@silica	Chlorantraniliprole	Site-specific delivery, crop nutrition	Insecticide	[52]
PDA@Dini@NH_2-MIL-101(Fe)	Diniconazole	pH-responsive	Fungicide	[158]
*DNF@MIL-101(Fe)@CMCs	Dinotefuran	Eco-friendly, double-coated, long-acting	Insecticide	[152]
AZOX@Dini@NH_2-MIL-101(Al)	Azoxystrobin, Diniconazole	Dual encapsulation, pH-responsive	Fungicide	[159]
*Tebuc@MIL-101(Fe)-TA	Tebuconazole	Gated nanocarrier, multi-stimuli-responsive	Fungicide	[51]
AZOX@ MIL-100 (Fe)	Azoxystrobin	Crop nutrition	Fungicide	[160]
Benguard@CuBTC	Benguard	96% encapsulation efficiency	Fungicide	[161]
AVM@CuBTC	Avermectin	Anti-photolysis	Insecticide	[51]
LC@UiO-66	Lambda-cyhalothrin	High loading, sustained release	insecticide	[146]
IMI@Fe_3O_4@PDA@UiO-66	Imidacloprid	Magnetic collectable	Insecticide	[162]
ATP@NH_2-UiO-66-CMC	Acetamiprid	pH-responsive, eco-friendly, high loading	Insecticide	[147]
**TMX@NH_2-UiO-66/SL	Thiamethoxam	pH-responsive	Rice pesticide	[163]
**CTD@UiO-66/Alg	Clothianidin	Dual stimuli-responsive, eco-friendly	Pesticide	[164]
**IDC@UiO-66-$(COOH)_2$-PNIPAm	Indoxacarb	Temperature-responsive, long-acting	Insecticide	[165]
Pro@Da@ZIF-8	Prochloraz	pH-responsive, light-triggered	Fungicide	[166]
DNF@ZIF-8@PMMA@zein[a]	Dinotefuran	Long-acting, crop nutrition, eco-friendly	Insecticide	[155]
Boscalid@ZIF-67	Boscalid	pH-responsive	Fungicide	[167]
KSM@ZIF-90	Kasugamycin	pH-responsive, multimodal antimicrobial	Fungicide	[168]
JGM@Zn2(EBNB)2(BPY)2.2H2O, AVM@$Zn_2(EBNB)_2(BPY)_2.2H_2O$	Jinggangmycin, Avermectin	Water soluble, oil soluble, sustained-release	Fungicide	[169]
AVM@γ-CD–MOF	Avermectin	pH-responsive	Acaricide	[170]

[a] Zein refers to corn protein
*The hybrid pesticide carriers are formed by inducing weak interactions
**The hybrid pesticide carriers are formed by covalent chemical bonding
Alg: Alginate CMCs: carboxymethyl chitosan Cs: chitosan
BPY: 4,4′-bipyridine CMC: carboxymethyl cellulose TA: tannic acid
PDA: polydopamine Da: 2,4-dinitrobenzaldehyde γ-CD: γ-Cyclodextrin
CMS: carboxymethyl starch PMMA: polymethylmethacrylate P: pectinEBNB: (E)-di (p-3-nitrobenzoic acid) ethylene PNIPAm: poly (N-isopropyl acrylamide)

delivery. Here, β-CD-NH_2 coating effectively prevented the photo degradation of indoxacarb. Moreover, this nanocarrier showed the controlled release of active ingredients (AIs) under acidic and amylase conditions. Therefore, the precise evaluation of nano pesticides and present commercial products is urgently needed.

Metal-organic framework as nano pesticides

The potential roles of MOFs in sustainable agriculture include detecting, removing, and controlling agrochemical release [137–139]. Therefore, the biological applications of MOFs have been extended to meet the need to effectively manage environmental hazards, particularly those related to the agriculture and the food industry. Despite the more widespread use of MOFs in detection [140–142] and elimination of pesticide residues [143–145], the applications of MOFs, particularly nanoscale MOFs, as pesticides have rarely been reported.

Herein, we will provide an overview of recent efforts to develop controlled-release formulations of MOF-enabled pesticides. As robust carriers for the controlled delivery of pesticides, MOFs or nano-MOFs (NMOFs) have recently attracted great interest due to their negligible premature release, lower toxicity to non-target organisms in soils, and high pesticide loading capacity [146,147]. The idea of MOF-based carriers for pesticides has emerged from the widespread use of MOFs for drug delivery applications. This is typically due to the unique characteristics of MOFs, such as adjustable structure and porosity, high BET surface areas, significant loading capacity, and high biocompatibility [148–150].

MOF-enabled nano pesticides have been developed as nanocarriers because of their superior encapsulation performance, tunable cargo release kinetics, and dynamic and reversible host–guest interaction potential [52,151]. To put it differently, the MOF-based nano pesticides include agrochemicals encapsulated within the MOF nanocarriers. They are primarily aimed at delivering nano pesticides by controlled release of AIs [152]. The protection of pesticides over photolysis and harsh environmental conditions, as well as high stability in aqueous media, is favored by using encapsulated formulations [153].

The eco-friendly MOFs or MOFs with renewable linkers (i.e., lactate, acetate, etc.) and non-toxic transition metals (i.e., UiO-66, Ca- and Fe-based MOFs, etc.) have been reported as promising candidates among MOFs for fumigant activity against agriculture pests [146,150]. In 2017, an MOF was synthesized through bridging the lactate ligand to Ca^{2+} ions via the carboxylate and hydroxyl groups, named as MOF-1201 [150]. A 1D pores having apertures of 7.8 Å and internal diameter of 9.6 Å provided 430 m^2/g porosity capable of encapsulation of cis-1,3-dichloropropene, an efficient fumigant. MOF-1201 released encapsulated pesticide 100 times slower than free the cis-1,3-dichloropropene. MOF-1201 easily dissolves in water and prevents accumulation in the soil, solubility of 120 g/L, while providing the necessary calcium for the plants. Furthermore, the MOFs containing essential mineral metals (e.q., Zn, Fe, etc.) can also act as a fertilizer to improve soil fertility and, subsequently, the productivity and quality of crops [154,155].

Table 3 lists the MOF-enabled pesticides reported in the literature, corresponding specifications, and the adopted approach for controlling pests and crop nutrition management. In some carriers, individual MOFs without surface coating and functionalization are involved in producing pesticide carriers by employing typical MOFs such as ZIF-8, ZIF-67 (Zeolitic imidazolate frameworks), MIL-101 (Materials of Institute Lavoisier-based framework), HKUST-1 (Hong Kong University of Science and Technology, also named MOF-199 or CuBTC), UiO-66 (University of Oslo, a Zr-based MOF), etc.

Despite the individual MOF pesticide delivery vehicles, some carriers comprise MOFs and biomass resources or natural polymer derivatives of chitosan, starch, chitin, cellulose, alginate, etc. The MOF composite carriers with hierarchical porosity are designed to produce hybrid systems exhibiting both controlled release and enhanced biosafety benefits attributable to the individual MOF and biomass resource [171]. The formation of core–shell structures enables the improved performance specifications of MOF-enabled pesticides, resulting in some cases in double-layered coated pesticides. Huang et al. [171] modified the porous HKUST-1 (MOF-199) surface with carboxymethyl chitosan (CMCS) via its carbocyclic, hydroxyl and amine functional groups and fabricated HKUST-1@CMCS log-last carrier for dimethyl fumarate. The chemical cross-linking the Cu metal ion with CMCS led to production of high stable carrier, which retained its MOF skeleton after release of its antibacterial agent. Therefore, HKUST-1@CMCS prevented the Cu^{2+} leaching and showed the recyclability features. This novel carrier can release antibacterial agent upon phosphate stimuli. The dimethyl fumarate- loaded HKUST-1@CMCS prevented the E. coli and S. aureus activity without efficiency decrement even after 7 days. The double-layered pesticides, as novel carriers with multi-functions, provide opportunities for long-acting pesticide delivery by sustained release and can act as fertilizer in crop nutrition. Gao et al. [52] introduced an intelligent nanocarrier (MIL-101 (Fe)@silica) with dual functionality for pest management. They loaded chlorantraniliprole (CAP) in pores of MIL-101(Fe), and then protected it via a silica shell. The CAP@MIL-101(Fe)@silica acted simultaneously as site-specific releaser of CAP and fertilizer. The slow release of Fe and Si provides nutrients needed for plant growth along with insecticidal activity. The CAP@MIL-101(Fe) @silica retained 86%of its mortality toward P. xylostella larvae after 14 days that was superior to 36.7% of the free CAP sprayed on plants. The shell layer can influence the responsiveness of hybrid carriers so that shell constituents respond to temperature, ionic content, etc., which is relevant for designing and developing controlled-release systems [164]. In addition to the stimuli responsiveness of the shell constituents in certain hybrid MOF-based carriers, the structure of certain MOFs can be independently influenced by various stimuli. The MOF structures respond to external stimuli, including pH, UV light, temperature, specific ions, etc., which develop stimuli-responsive MOFs [167]. The stimuli-responsive MOFs are used to achieve an intelligently controlled release system with targeted delivery of AIs and prevention of environmental pollution. Zhang et al. [167] constructed a pH-responsive nano pesticide to destroy citrus agent of Botrytis cinerea (Fig. 5). The Boscalid encapsulated in the ZIF-67-based nano carrier was released in a controlled manner via pH adjusting. The plant infection by Botrytis cinerea leads to citric acid production that rapidly triggers the Boscalid release.

The hybridization of MOFs and other components is conducted by surface coating through weak interactions (i.e., electrostatic interaction, physical adsorption), so-called layer-by-layer assembly [156], and surface covalent bonding methods [153], including in situ polymerization [155], and chemical cross-linking [164]. An AZOX@MIL-100 (Fe) pesticide with pH-sensitive behavior resulting from the particular structure of MOF was developed [160]. In acidic conditions, the carboxylic acid groups (–COOH) of MIL-100 formed hydrogen bonds with AZOX, resulting in a slow release and non-Fickian transport. However, in neutral or alkaline conditions, pesticide release was facilitated by a quasi-Fickian diffusion mechanism attributable to the deprotonation of carboxylic acid groups and the subsequent absence of hydrogen bonding. The results showed that kinetics and mechanisms of pesticide release were influenced by pH value in the pH-dependent structure of the individual MOFs [160].

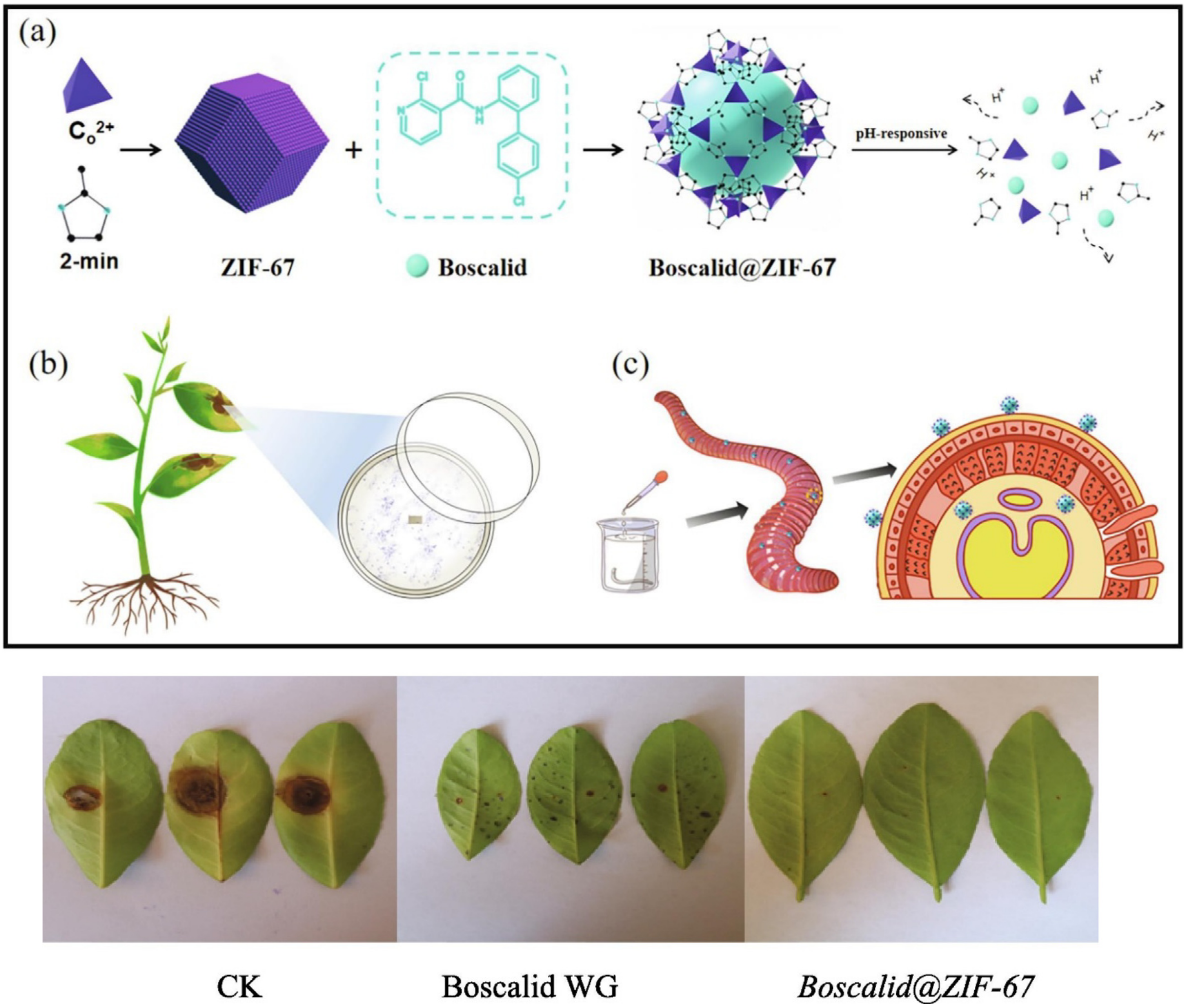

Fig. 5. Up: (a) the 3D structure and synthesis procedure of Boscalid@ZIF-67 and triggered-release mechanism of Boscalid, (b) the bacteriostatic impact of Boscalid@ZIF-67 on Botrytis cinerea, and (c) the portrait of the Boscalid@ZIF-67 killing effect on earthworms. Adopted with permission from [167].

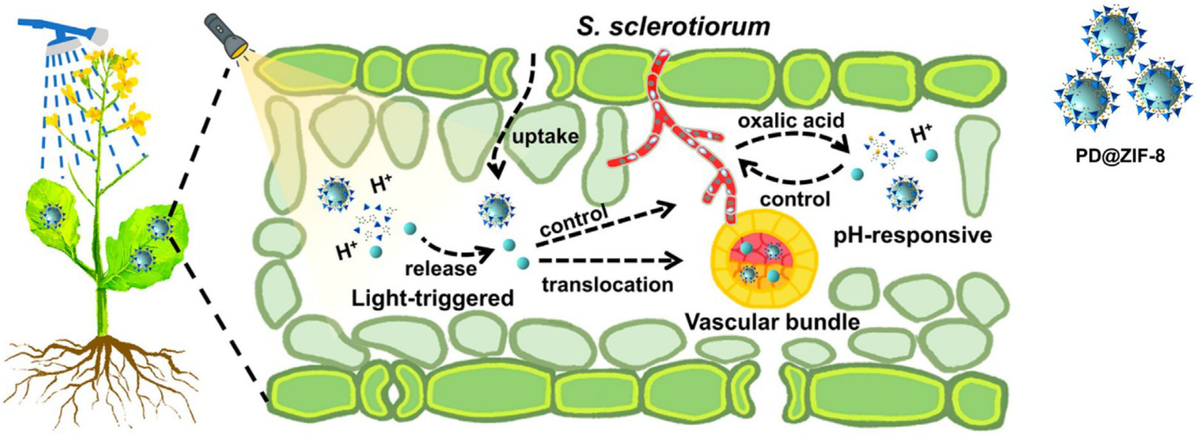

Fig. 6. Illustration of smart controlled release system of a MOF-enabled pesticide with multi-stimuli-responsive performance (i.e., light-triggered and pH-responsive). Adopted with permission from [166].

Despite the sensitivity attributed to the structure of MOFs, the pesticides can also be triggered by stimuli-responsive reagents, which encapsulate within the MOF-enables pesticides. For instance, adding a pH-jump reagent to the pesticide carrier induces pH-dependent degradation of MOFs under acidic conditions (Fig. 6) [166]. The stimuli responsivity can provide long-acting pesticide

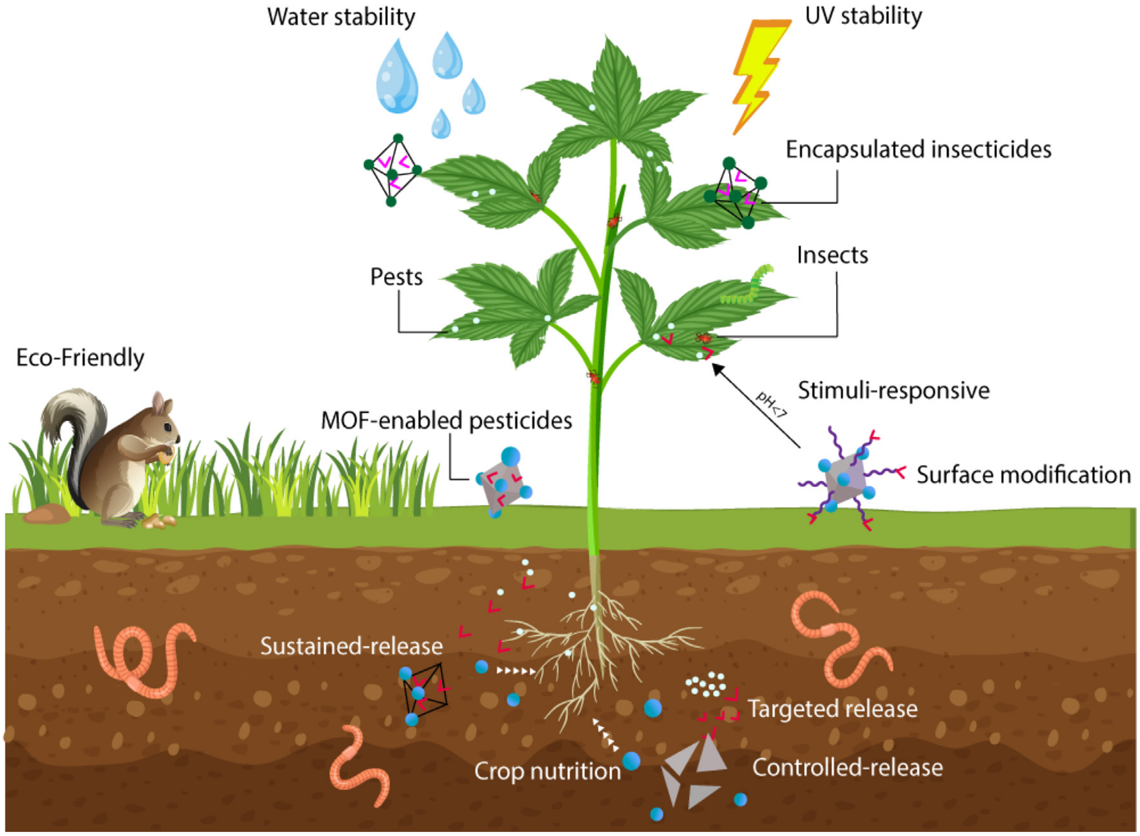

Fig. 7. Scheme illustration of the advantages of MOF-enabled pesticides from different points of view in controlled delivery systems.

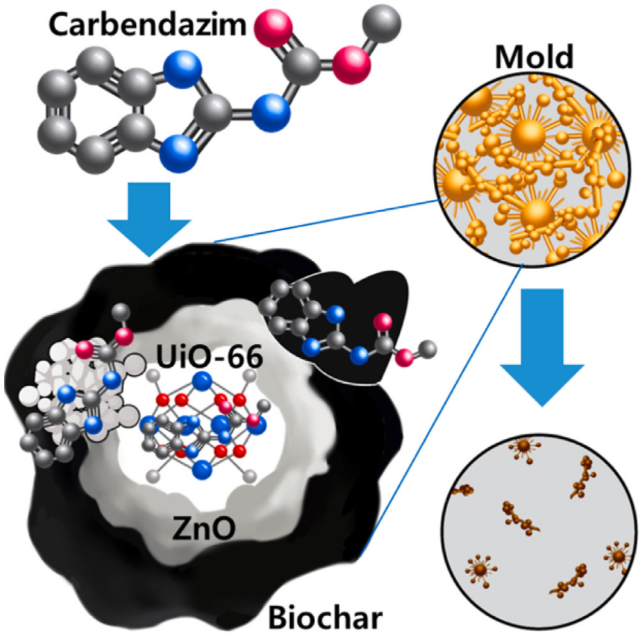

Fig. 8. The incorporation of CBZ in porous structure of nano UiO-66@ZnO/Biochar through efficient adsorption applicable for controlled release of CBZ in agriculture. Adopted with permission from [183].

release and more effective protection by preventing the burst release identified in other carriers (e.g., polymer-based carriers) [172,173].

The degradation of the carrier or the failure of the gatekeepers in gated MOF-based pesticides, which depend on the intrinsic properties of carriers, causes the release of the encapsulated pesticide. Regarding MOF integrity loss, both the linker decomposition and cleavage of coordination bonds between metal nodes (secondary building units) and ligands lead to the release of pesticides [166,167,174]. Failure of the gatekeeper occurs in gated carriers, specifically MOFs containing coordination unsaturated metal sites (CUSs, also known as open metal sites), which provide open metal sites and act as Lewis acid. CUSs were initially developed for gas adsorption, but subsequent research has revealed their promising applications in catalysis, storage, separation, etc. [175–177]. These open sites indicate the potential for functionalization and hybridization to anchor different functional units to the MOF surface [178]. For example, MIL-101 (Fe^{III}) gated with Fe^{III} and tannic acid (TA) networks as gatekeepers were developed [51]. These networks are formed by covalently linking the TAs to Fe^{III} unsaturated sites on the surface of nanocarriers encapsulated with fungicide tebuconazole. The cargo release was triggered by seven stimuli (acidic pH, alkaline pH, H_2O_2, GSH, phosphate, EDTA, and sunlight), followed by the partial disassembly of Fe^{III}-TA networks and by a gradual release of fungicides [51].

Advantages

Due to their unique properties, porous crystalline MOFs are among the most promising candidates for controlled and sustained pesticide release. MOFs with hierarchical structures used as pesticide delivery vehicles increase encapsulated pesticides' water stability and anti-photolysis properties to protect them from environmental degradation (Fig. 7), demonstrating that MOF-enabled pesticides improve the development of eco-friendly innovations [179,180]. As a result of the MOF carriers' enhanced capability to anchor the pesticides on the surface of leaves and plants, encapsulated pesticides show enhanced adhesion compared to free pesticides [165]. The capability of MOFs for diverse surface modifications and functionalization, especially covalent grafting of polymers, is advantageous to the pesticide/drug loading performance and plays a crucial role in preventing pests and plant diseases [181,182]. As was mentioned before, changing the intensity or type of stimuli presented to the stimuli-responsive MOFs can improve their ability to control the pests.

Recently, an MOF-based nanocomposite named UiO-66@ZnO/Biochar was synthesized to incorporate carbendazim (CBZ) pesticide inside its porous structures [183]. This was done to enable intelligent spraying and promote more environmentally friendly production methods. The preparation strategy was depicted in Fig. 8. Utilizing the UiO-66@ZnO and UiO-66@ZnO/Biochar samples led to achievement of 68.8% and 72.6% loading efficiency for CBZ, respectively. The CBZ molecule effectively adsorbed by UiO-66@ZnO/Biochar via electrostatic and aromatic π-π interactions. The presence of biochar in nanocomposite structure enhanced adsorption capacity of CBZ while decreased the required time to 24 h. Moreover, the experiments on release efficacy revealed a pH dependence behavior as the CBZ releasement for pH 5.0 condition reached to at least 78% after 24 h, while only 45.4% and 29.2% CBZ discharge was resulted under pH values of 7.0 and 9.0, respectively. The anti-fungal effect of CBZ@UiO-66@ZnO/Biochar was examined through growth prohibition of Aspergillus niger and Fusarium oxysporum, which provided inhibitory concentration 50% (IC50) amounts of 209 μg/mL and 73.8 μg/mL, respectively. The reduced IC50 CBZ@UiO-66@ZnO/Biochar compared to untreated CBZ, leads to application of less amount of active ingredient in fields. The results propose the possible utilization of the UiO-66@ZnO/Biochar in intelligent application of the CBZ pesticide, aiming to enhance spraying efficiency and ensure precise delivery of the pesticide to the plants. Ultimately, this approach aims to minimize the amount of pesticides reaching underground water sources, leading to a reduction in overall pesticide usage.

Deltamethrin (DM), known for its effectiveness as an insecticide, exhibits significant toxicity against mosquitoes, flies, and aphids. However, the use of traditional DM formulations in agriculture gives rise to significant issues such as sudden release, limited persistence, inadequate insecticidal efficacy, and substantial environmental contamination. To address the limited efficacy of traditional pesticide formulations, the use of a pesticide delivery system (PDS) has proven to be an effective solution. Wan and colleagues [184] explored the application of UiO-66, a novel MOF-based nanocarrier, for loading DM (an active ingredient) through a process known as physical adsorption. By utilizing DM@UiO-66 as a PDS, they were able to create a stable nano formulation that facilitated sustained release of DM, thereby enhancing pest control. Unlike conventional formulations that release the pesticide rapidly, DM@UiO-66 demonstrated a prolonged release performance, enabling the maintenance of an effective insecticidal concentration over an extended period. Furthermore, DM@UiO-66 is environmentally friendly, as it does not contain any toxic organic solvents or additives. The BET analysis was used to determine the specific surface area and porosity of UiO-66 and DM@UiO-66. UiO-66 possesses a microporous structure with a loading capacity of 1049.6 mg/g for DM. According to the BET results, UiO-66 has a specific surface area of 1021.79 m^2/g and a total pore volume of 0.52 cm^3/g. After DM loading, the pesticide molecules occupy the mesoporous structure of UiO-66, resulting in a reduction in specific surface area and total pore volume for DM@UiO-66 to 354.29 m^2/g and 0.16 cm^3/g, respectively. In terms of release, the cumulative amount of DM released reaches approximately 80% within 10 hours for the free DM group, while it is about 55% for DM@UiO-66. DM@UiO-66 exhibits a slow-release performance compared to free DM, allowing for sustained release of the active ingredient into the medium. The release of DNM from the nano formulation of DM@UiO-66 followed the Kitger-Peppas equation. The calculated diffusion index, n, was 0.54 (0.45 < n < 0.85), suggesting that the diffusion mechanism of DM from the nanocarrier is non-Fickian in nature. The water contact angle of the DM@UiO-66 nano formulation was assessed. It was observed that DM@UiO-66 exhibited a water contact angle of 88° on maize leaves, which was smal-

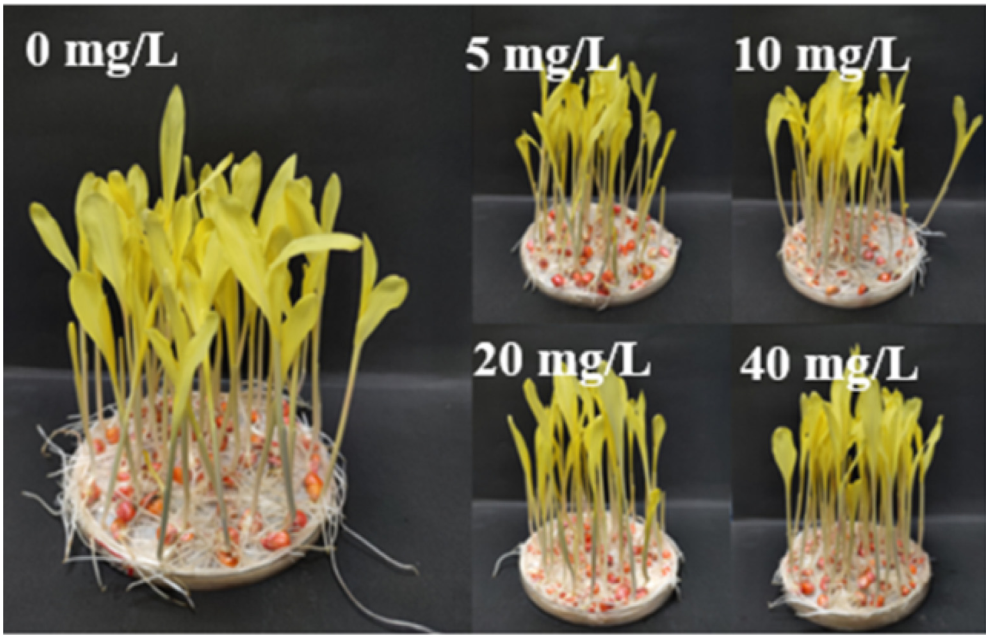

Fig. 9. The impact of various concentrations of DM@UiO-66 on the germination rate of maize. Adopted with permission from [184].

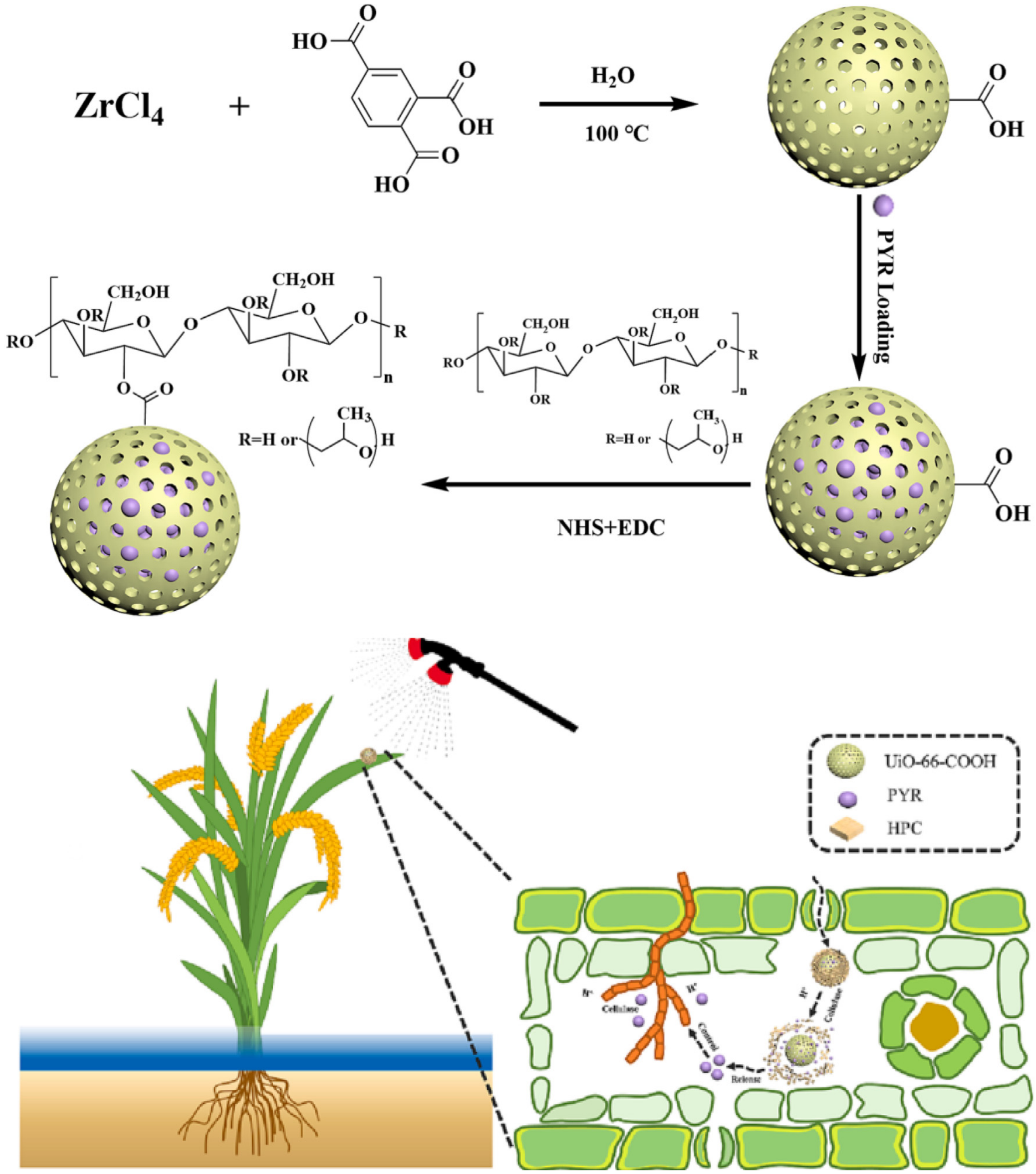

Fig. 10. A) Proposed strategy for the synthesis of PYR@UiO-66@HPC and (B) Release mechanism of PYR stimulated in plants via infestation by pathogenic bacteria. Adopted with permission from [185].

ler than that of free DM (116°). This indicates that DM@UiO-66 has improved leaf affinity and wettability. Consequently, compared to free DM, the UiO-66 nanocarrier effectively enhances the adhesion rate of DM on leaf surfaces, thereby benefiting the antipest activity. The DM@UiO-66 nano formulation demonstrates superior insecticidal activity compared to free DM, attributed to its enhanced leaf affinity and slow-release performance. To preliminarily assess the biosafety of the DM@UiO-66 nanoformulation, the germination rate of maize seeds and the growth of maize seedlings were examined (Fig. 9). The germination rate of maize seeds treated with the DM@UiO-66 nano formulation remained at approximately 100% compared to the control group, indicating no adverse effects on maize seed germination.

Rhizoctonia solani poses a threat to rice fields, leading to decreased yields and potential crop loss. Pyraclostrobin (PYR), a potent fungicide, has demonstrated effective protection against this disease in rice fields. However, the high toxicity of PYR to aquatic organisms restricts its practical application in aquatic environments. During infestation, Rhizoctonia solani releases oxalic acid and cellulase to facilitate the rapid degradation of plant cell walls. Therefore, the utilization of localized low pH conditions and elevated cellulase concentrations could be considered as potential stimuli for PYR release. This approach aims to enhance pesticide effectiveness and minimize associated risks. Ma et al. [185] developed a controlled-release pesticide formulation that responds to both pH and cellulase stimuli (Fig. 10A). This formulation involves loading PYR into the UiO-66 MOF and then applying a layer of hydroxypropyl cellulose (HPC) as a coating, (PYR@UiO-66@HPC). The desired control effect was achieved through the breakdown of ester bonds in acidic conditions and the enzymatic

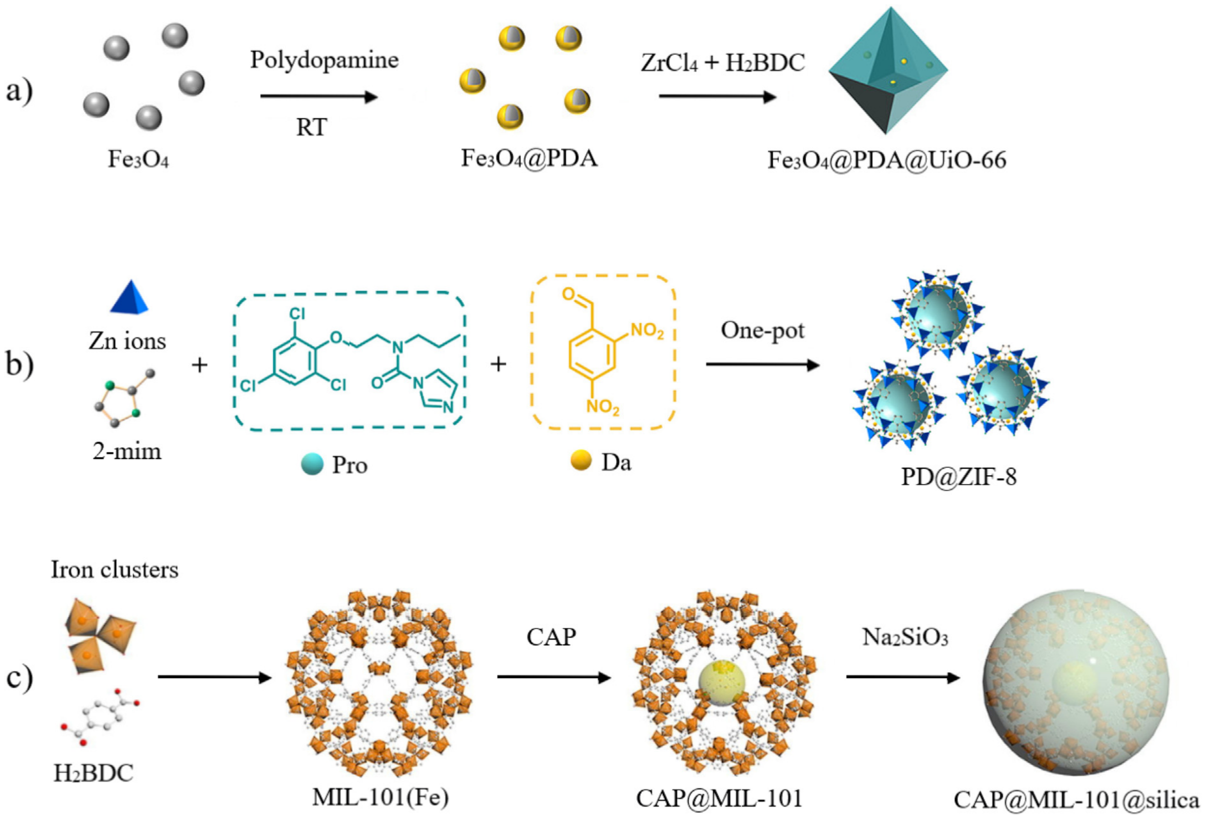

Fig. 11. Scheme illustration of hybrid carriers prepared using a) pre-hybridization (Adopted with permission from [162]), b) in-situ-hybridization (Adopted with permission from [166]), and c) post-hybridization methods (Adopted with permission from [52]).

hydrolysis facilitated by secreted cellulose. The attachment of PYR to the pristine UiO-66-COOH composite led to decrement of surface area from 221.64 m^2/g to 149.35 m^2/g, which can be attributed to the occupation of composite pores by PYR. Similarly, the grafting of HPC resulted in the sealing of pores, leading to a similar observation. The dual stimulatory response properties of PYR@UiO-66@HPC towards pH and cellulase facilitates faster release of the pesticide during pathogen infestation and as a result achieving higher inhibitory activity (Fig. 10B). The potential harmful effects of PYR@UiO-66@HPC on D. magna, a commonly used model organism, were assessed in terms of acute toxicity. The EC50 value of PYR@UiO-66@HPC was approximately 4.6 times higher than that of PYR-TC, even after a 48-hour exposure period, indicating its superior safety profile. This was attributed to the protective nature of PYR@UiO-66@HPC, where the PYR compound is encapsulated within UiO 66@HPC, preventing direct contact with D. magna, unlike PYR-TC.

Synthesis

The synthesis and evaluation of MOFs based nano pesticides involve a series of steps: i) *MOF selection*. First, a suitable MOF that can efficiently encapsulate the pesticide molecule must be chosen based on pore size, stability, and compatibility with the pesticide molecule; ii) *MOF preparation*. The MOF is synthesized using methods and conditions optimized to obtain particles with the desired properties; iii) *pesticide loading*; iv) *characterization* to confirm the successful encapsulation of the pesticide molecule and to determine the physical and chemical properties of the nano pesticide; v) *efficacy evaluation* through bioassays on target pests under controlled conditions to evaluate the toxicity, selectivity, and persistence; vi) *optimization*. The MOF-based nano pesticide formulation is optimized by varying parameters such as loading efficiency, concentration, and release kinetics.

Broadly speaking, individual MOFs have been synthesized through various methods, such as hydro/solvothermal [186], microwave [187], sonochemical [188], room temperature [189], and others [190]. Research efforts have also been devoted to the green synthesis of MOFs without using hazardous chemicals, which is beneficial for potential food and agricultural applications [191,192]. Most reported MOF-enabled pesticides are obtained via solvothermal synthesis using a Teflon-lined autoclave reactor. The reaction is performed above the solvent's boiling point over several hours or days by heating in an oven [146]. In some instances, MOFs can be easily prepared by combining the reflux synthesis with magnetic stirring over a period of time, followed by separation by centrifugation [164].

The AIs can be deposited on the delivery vehicles by different loading methods and loaded pesticide/MOFs interactions, including physical adsorption, covalent attachment through ligands, encapsulation, and entrapment [193]. The pesticides are loaded into delivery carriers with either one-step or stepwise approaches, which refer to in-situ- and post-loading. Specifically, the in-situ loading of pesticide species into MOF pores occurs during framework assembly, whereas the MOF structure is fully formed before pesticide loading in the post-loading method. Regarding the former, solid MOFs or MOF solutions are typically soaked, suspended under stirring, or dissolved in pesticide solution by dropwise addition at room temperature for 24 hours or more [52,146]. For example, Liang et al. prepared ZIF-90-kasugamycin (KSM) pesticide through a Schiff base reaction [168]. The reaction was carried out by dropwise adding the ZIF-90 buffer solution to a buffer solution containing KSM with continuous stirring. A pH-sensitive property was observed in the corresponding pesticide because of the Schiff base bonds between KSM and ZIF-90, which decomposed at acidic pH, and the carriers were dissolved completely [168].

Pre-, in-situ-, and post-hybridization methods have recently been proposed for preparing hybrid carriers derived from MOFs (Fig. 11). Physical interactions (i.e., physically cross-linked) between natural polymers and multivalent ions as the metal source for forming MOFs cause pre-hybridization. The metal cross-linked polymer networks serve as a precursor for the formation of MOF, which begins at the cross-linked sites and is completed with the help of organic linkers (Fig. 11a) [162,194]. On the other hand, the in-situ hybridization of MOF-based carriers is defined as the simultaneous formation of MOFs and functionalization with biomass resources using a one-pot method to prepare hybrid carriers in one step (Fig. 11b) [166]. Regarding post-hybridization, the carriers can be synthesized by adopting a core-first approach, which refers to forming MOF before the hybridization step (Fig. 11c). Notably, hybridization is performed after AI loading to protect MOF-enabled pesticides from environmental hazards and prevent poisoning by decreasing exposure [52,155].

Challenges and modifications

Considering the ecotoxicological aspects of nano pesticides, MOFs' green synthesis and modification capabilities result in non-hazardous nano-pesticides' formation, thereby reducing toxicity and environmental impacts. Despite the extensive development of MOFs, the majority of synthesized MOFs are constructed using transition metal ions and organic linkers obtained from petrochemical sources. Regrettably, their harmful nature has hindered numerous crucial applications that demand environmentally friendly materials, for instance, in the food industry, biomedicine, and agriculture. Synthesis based on non-toxic and environmentally friendly metal ions and natural linkers can widen the scope of the MOF's application. It is still difficult to achieve their synthesis [150]. The reason for this difficulty lies in the numerous coordination arrangements and the high number of coordination bonds formed by harmless metal ions like calcium. Additionally, the flexibility of natural organic connectors adds to the complexity, resulting in the formation of compact structures lacking pores. However, despite being biodegradable, certain MOFs must be modified before their efficient biological applications [150]. When is desirable to reduce the toxicity of MOFs for the benefit of microorganisms, changing as-synthesized MOFs can be a crucial detoxification step.

White-rot fungi, which play a crucial role as decomposers in the carbon cycle, are of significant interest and importance due to their ability to specifically break down lignin-containing biomass.

White-rot fungi have the ability to produce enzymes such as laccase, manganese peroxidase, and lignin peroxidase, which can break down lignin. This process leads to the conversion of wood and straw into humus, and eventually the release of carbon dioxide back into the atmosphere. White-rot fungi's strong oxidative abilities also make them suitable for pollutant remediation. However, the potential toxicity of MOF materials towards fungi, as suggested by some initial studies, raises concerns. If MOF materials interfere with the decomposition ability of white-rot fungi, the carbon-containing biomass may not decompose as expected, resulting in a disruption in the carbon cycle. To understand the environmental risks of MOF materials and develop detoxification methods, it is crucial to investigate their effects on white-rot fungi, which serve as representative microorganisms. For instance, Ma et al. [195] synthesized the green MOF-199, which was carbonized by annealing in a tubular furnace to lower the release of Cu^{2+} ions, indicating oxidative decomposition activity. At a concentration of 100 μg/mL, MOF-199 effectively stopped the activities of laccase and manganese peroxidase. Additionally, it reduced the decomposition activity of P. chrysosporium, as observed by the decrease in the decolorization of reactive brilliant red X-3B. On the other hand, carbonized MOF-199 had minimal impact on the enzyme activities and decomposition capability.

The inability to reach the effective concentration of pesticide in pest control is a difficulty associated with controlled release, which is caused by the slow-release behavior of MOF-based pesticide carriers during the early release stage. To achieve the long-term

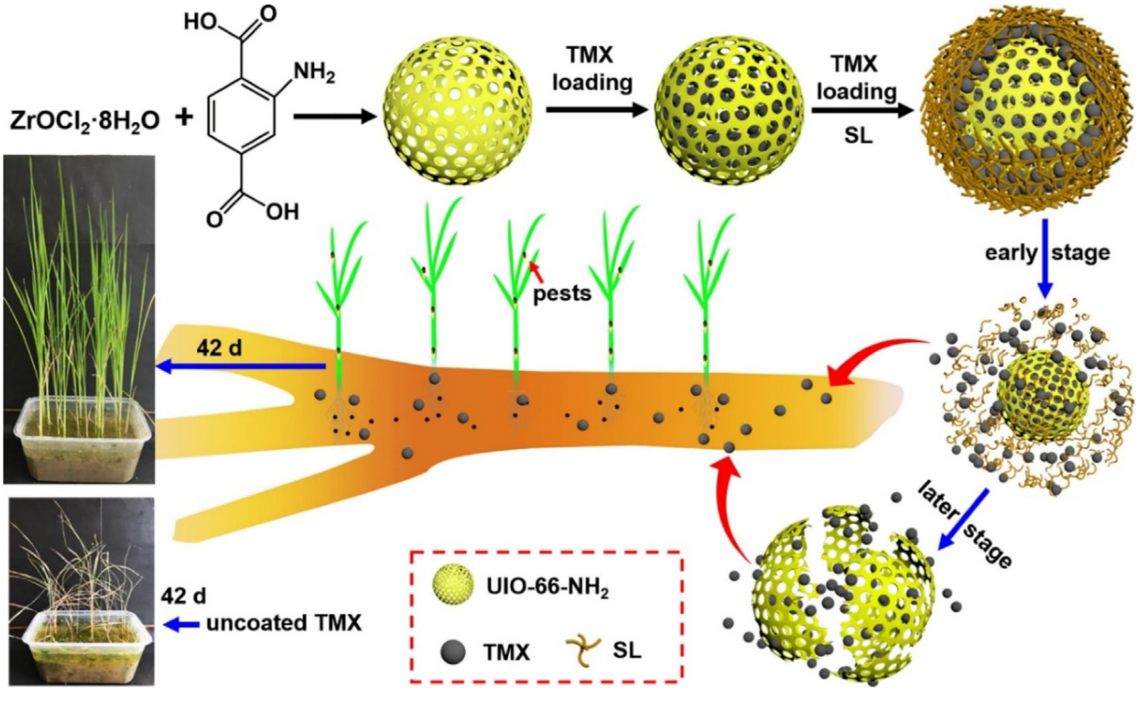

Fig. 12. Schematic representation of TMX-loaded UiO-66-NH_2/SL synthesis and pest control at early and later stages of rice growth. Adopted with permission from [163].

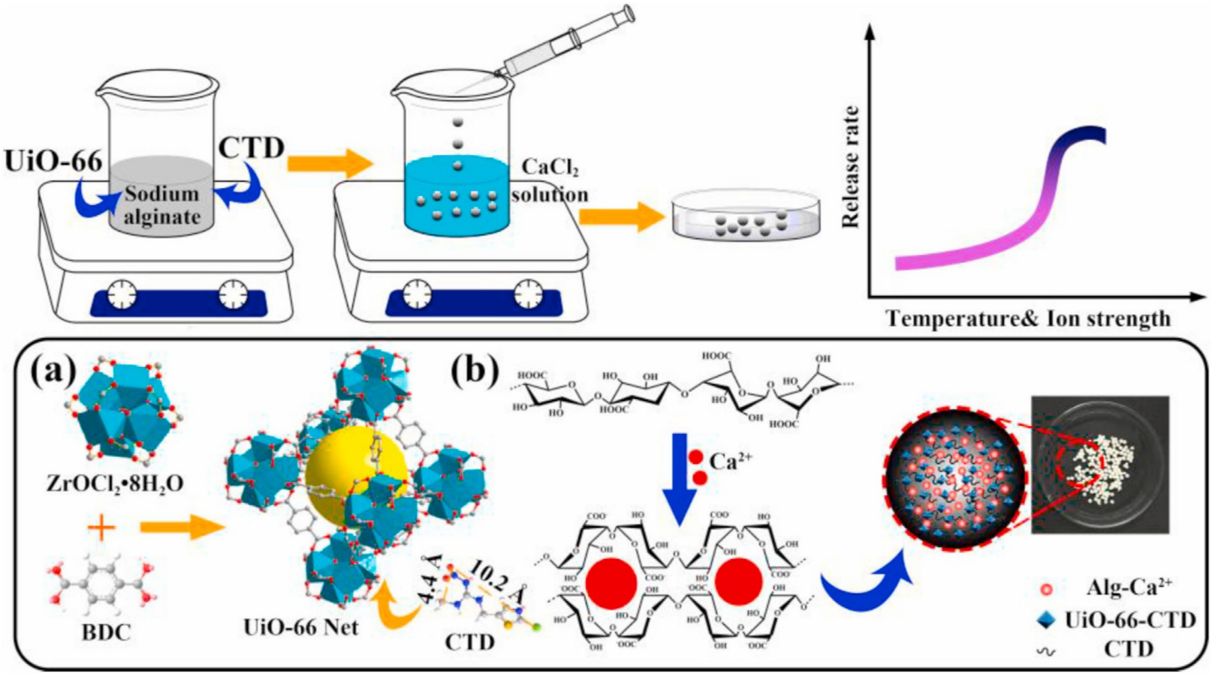

Fig. 13. The formation process of (a) UiO-66 and (b) CTD@UiO-66/Alg micro spherical-shaped through ion cross-linking reactions. Adopted with permission from [164].

effects of thiamethoxam (TMX) on the soil microbial community, Huang et al. [163] constructed a double-layer pesticide carrier of UiO-66-NH$_2$/sodium lignosulfonate (SL). TMX was loaded in the outer layer between MOF and SL and the pores of UiO-66 that they released in early and later stages, respectively (Fig. 12). Hence, the release time of TMX-loaded UiO-66-NH$_2$/SL in soil was 8 times longer than uncoated TMX and exhibited an improved effect on rice pests [163].

Similarly, Feng et al. [164] developed a novel hybrid pesticide carrier consisting of UiO-66 and sodium alginate (Alg) to safely release clothianidin (CTD). The CTD encapsulation in UiO-66/Alg was done via a chemical process. The CTD@Alg@UiO-66 hybrids with double stimuli-responsive exhibited controlled-release pesticide formulations that respond to changes in both temperature and phosphate concentrations. The formulated nanocarrier was able to deliver 62.74% and 93.52 % loaded CTD at 27 and 45 °C, respectively. The CTD@UiO-66/Alg showed more than 3.5 times UV-resistance than free CTD. The smart-ion controlled release of CTD@UiO-66/Alg is stimulated by phosphate ions. Fig. 13 depicts the synthesis process of UiO-66/Alg and CTD loaded MOF. In addition, biological tests of CTD@UiO-66/Alg on E. coli and rice seeds confirmed the biosafety of prepared nano pesticide and its promising pest manengment ability for agriculture utilization.

Nano pesticides and sustainable agriculture

Pesticides are currently an indispensable component of agrochemicals for sustainable and secure agriculture [196,197]. Due to the continuous expansion of human civilization and the consequent rise in demand for high-value agricultural products, many efforts have been made to develop safer and more effective pesticides. The significance of developing a comprehensive pesticide regulation has been examined from two primary perspectives: minimizing environmental risks associated with pesticide contamination and utilizing effective pesticides for crop production and protection [198]. However, traditional pesticide formulations suffer from several disadvantages of toxicity, poor stability and water solubility, uncontrolled (burst) release of AIs, and potential risks to non-target organisms [199], limiting their practical applications in sustainable agriculture. In this context, nano-enabled pesticides support the advancement of sustainable agriculture [102,200,201] by efficiently managing pests and enhancing crop nutrition [143,202,203].

As agrochemical delivery vehicles, the nanocarriers are used for smart and targeted AI delivery, minimizing pesticide residues and increasing water stability and solubility [204–206]. Many nano pesticides are either metal-based or carrier-based. Even though nanometals have been used directly as pesticides due to their antimicrobial activity, their usage has decreased in recent years due to the safety concerns attributed to the toxic and heavy nanometal use [207–209]. Distinctively, various the development of encapsulated pesticides showed a rising trend, with strategies including polymeric nano carriers (e.g., starch, chitosan, lignin, etc.) [210,211], inorganic nanoparticles (e.g., clays, zeolites, metals, etc.) [212,213], and nanocomposite carriers (e.g., organic@inorganic materials, MOFs, and MOF composites) [52,214,215].

The effect of metal chelation on nanocarriers can be observed in inorganic and nanocomposite carriers, which, by introducing metal coordination bonds, can facilitate the transport of pesticides. Competitive coordination of pesticides and protons with metal chelation results in a pH-responsive nano carrier for the triggered release of cargo. Moreover, the release of pesticides can be regulated by the presence of the gatekeepers, which is attributed to the coordination of metal cations [216].

The composite nano carriers combine the advantages of both organic and inorganic components, and thus high efficiency of crop production and protection at low pesticide concentrations are achieved. Among the various nanocomposite carriers developed in recent years, MOF is used to meet the requirements of sustainable agriculture and environmental remediation as a biodegradable pesticide delivery vehicle. As previously stated, this is due to its promising pesticide delivery characteristics, such as slow release, eco-friendliness, enhanced pesticide interaction, strong leaf adhesion, etc. Even though MOF-enabled pesticides still face regulatory challenges, future research opportunities exist to address pesticide use limitations.

Conclusions

This work presented a bird's eye view of state of the art in the area of nano-pesticides, focusing on the application of MOFs as sustainable and effective carriers. In the context of increased worldwide pollution, pesticide accumulation and high regulatory demands, the need for viable, efficient and green pesticides that can sustain agricultural productivity and ensure reasonable pest control are in stringent need. Nano pesticides, in general, and MOF enable nano pesticides, in particular, to respond to this challenge by a controlled and sustained pesticide release, reduced use of toxic and harmful AI, and targeted delivery. Moreover, their flexibility in design and capability to modification and hybridization indicate excellent potential for development. However, as the use of MOFS as carriers for pesticides is in its early infancy, attention must be paid to the potentially toxic effects, and further research is required to determine their environmental impact and improve their performance.

The new development directions can be focused on solving the challenges associated with the optimized controlled release and carrier performance. Size and shape are determinants of AI payload capacity and, consequently, performance and can be modified through various carrier preparation and AI addition techniques. Hence, the structure designability of MOF-enabled pesticides opens a window of opportunity to obtain pesticides with desired properties in terms of cargo payload capacity, release rate and duration, structural durability, economic efficiency, and environmental impacts. During the following years, it is anticipated that further efforts will be devoted to achieving comprehensive, effective pesticides taking into account the simple and low-cost preparation process, mitigating the overuse of pesticides, and finally, excellent delivery performance.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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