Polymeric Nano-insecticides: Latest Innovations, Environmental Impacts, and Future Aspects

Annika Singh[1], Mukesh Kumar Singh[2], School Of Life Sciences and Biotechnology, CSJMU Kanpur[1], UPTTI, Kanpur[2]

Abstract

The increasing demand for food is compelling farmers to protect crops from diseases and pests through the overuse of insecticides. Although, the extravagant use of pesticides threatens human health and the environment. One promising solution for the safer use of pesticides is the application of nanotechnology, to increase agricultural production without these adverse consequences and lessen health and environmental side effects. This condition enhances the exigency of creating controlled-release nanocarriers to increase the pesticide earmarking, stop the early release of pesticides and minimize the side effects. Nanopesticides (NPs) are nanostructures carrying active agrochemical ingredients (AI). Nanopesticides possess higher surface area, allowing proper contact with pests, and making them more efficient than conventional methods.

Keywords: Nanocarriers, Engineered Nanopesticides, Active ingredients, unmanned aerial vehicles, NPs.

Introduction

The ever-increasing Global population requires quality food production equivalent to people's needs. The increasing use of chemical fertilizers, pesticides, and other agrochemicals is associated with economic investment in agricultural commodities, to improve productivity. However, intense and unsystematic use of chemicals results in an ecological imbalance in terms of reduced nitrogen fixation and biodiversity, pathogen resistance, and bioaccumulation of pesticides in agricultural, livestock, and aquatic biomass, which ultimately causes a severe and progressive threat to the ecosystem. The application of nanotechnology to allow safer use of pesticides is a promising solution, to increase agricultural production without these adverse consequences and lessen health and environmental side-effects. Any object which has a size range from 1 to 100 nm dimension is considered Nanomaterial. Nanomaterials exhibit some specific properties like size, shape, and composition (Gebre and Sendeku 2019).

Nanopesticides /insecticides are more effective because of their control release and high selectivity due to surface modification. Synthetic pesticides are formulated in nanomaterials by fixing on a hybrid substrate, encapsulation of NPs in a matrix, or utilizing functionalized nanocarriers for external stimuli or enzyme-mediated triggers, to find safe applications in the agricultural field. Several materials like silica, lipids, polymers, copolymers, ceramic, metal, and carbon can be used as matrices or nanocarriers for NPs AI [Agostini,, 2012]. The tiny size and large surface area stimulated the plant leaves' absorption and carrying of insecticides.

NPs deposited on or adsorbed by foliar parts or roots of plants, penetrate the outer epidermal layer, and are then transported to various parts of the plants through the vascular tissues. The NPs formulations may add some physicochemical properties like water solubility, and bioavailability. Nanostructure formulation also protects agrochemicals against environmental degradation, revolutionizing the control of pathogens, and insects in the crops [Yadav, R.K, et al. 2020]. However, the cytotoxicity and genotoxicity features of the nanomaterials are the major limitation.

It has been reported that dendritic macromolecular polymer nanocarriers with perylene imide can quickly penetrate the cell wall of the plant root cap and enter the plant cell. They can self-assemble fluorescent nuclei into complexes and hence can easily penetrate the intestinal epithelial membrane, and the other part of the body wall of pests and enter various tissues and cells of insects (He et al., 2013; Zhang, Colleen et al., 2022).

Nanopesticides

Nanopesticides are generally classified into two types by analysis of approximately 36,658 patents, (i) organic molecular active ingredient (AI)-nanocarrier complexes (polymers) and (ii) inorganic nanoscale AI without carriers.

Type 1 nanopesticides

In Type I NPs, nanomaterials (NMs) are directly used as AIs. The widely used Type I NPs are Metal-based NMs which include Ag, Ti, Cu, Zn, Fe, and Al-based NMs, as nano bactericides, nanofungicides, and nano insecticides.

Type 2 nanopesticides,

NMs serve as nanocarriers to encapsulate AIs to achieve controlled, targeted, and synchronized release of AIs at the right target, time, and dose e.g., $Cu\ (OH)_2$ nanopesticides. In the present chapter, we will discuss Type 2 Nanopesticides.

Polymeric Nanoinsecticides

Polymeric shells are a pretty promising solution for the controlled delivery of nanoinsecticides. These shells vary in size from 1-1,000 nm (Nuruzzaman et al., 2016).

Environment-affable polymeric solutions are more auspicious to work as active substance (AS) carriers owing to their biodegradable, biocompatible, non-toxic potential. Polymeric nano insecticides are suitable to minimize the quantity and application frequency due to the controlled release profile of AS.

The effectiveness of polymeric nano-formulations can be further enhanced by introducing controlled release and appropriate adhesives (Lowry et al., 2019). Polymeric nano insecticides can be delivered on the targeted zone by electrospun nanofibers, micelle, nanocapsule, nanogel, and nanosphere (Contreras-Cáceres et al., 2019).

Polymeric insecticide carriers

Many research groups are actively exploring the commercially viable solution for plant protection by using polymeric insecticides. The increasing awareness of sustainable developments is the main driving force to explore more and more natural and synthetic polymeric substances to be used as nano-insecticide carriers. The essential attributes of these polymeric materials are easy biodegradability, should not leave any carbon footprint after degradation, free from toxicity and cost-effectiveness.

Natural Polymers

The non-biodegradability of synthetic polymers guided the scientific community to explore natural polymeric materials, which have sustainable production and degradation cycle, and easy availability to be used as nanocarriers of insecticides.

Chitosan

Chitosan is a deacetylated product of chitin, the prime constituent of the invertebrates and exoskeleton of some bacteria, crabs, and fungi. The biocompatible, biodegradable, and toxic-free nature of chitosan drives it to be selected for controlled release on nano-insecticides.

In the last couple of years, chitosan has been used frequently as a carrier to manufacture insecticidal essential oils containing nanogels. The chitosan has enough functional groups in its polymeric backbone to impart additional attributes.

Alginate

The alginate is sourced from brown macroalgae, finding its application in the insecticide industry in the Alginate polysaccharides form. Alginate polysaccharides have the property of not accumulating in any human organ. The alginate polysaccharides are used in insecticides by an ionotropic gelification process controlled by metal ions. Sodium alginate is used with other polymeric substances such as chitosan, starch, and polyethylene glycol (PEG) to conquer the concerns related to the rapid release of active substances.

Cellulose

Cellulose, an overflowing natural polymer, has features such as biodegradability, biocompatibility, low toxicity, and low cost, which guide its use as a delivery system for many active substances. Numerous bacteria and fungi can decompose cellulose and its derivatives, making it an appropriate carrier for nano insecticides. However, very little research work is focussed on in this section. Starch is among the most energy-storage molecules of many glucose units found in fruits, grains, legumes, and roots. However, the weak water solubility of pure starch makes it challenging to use for various applications.

Various physical and chemical modifications of starch make it suitable for nano insecticide formulations.

Cyclodextrin

Cyclodextrin is a modified product of starch manufactured by enzymatic degradation consisting of a macrocyclic ring of 6, 7 and 8 glucose sub-units called α, β, and γ-cyclodextrins, respectively. The unique structure of cyclodextrins consists of a hydrophilic, polar outer surface with a hydrophobic inner pocket (Campos et al., 2015), which permits to form of non-covalent complexes with different hydrophobic compounds and modifies the biological, chemical, and physical behavior of attached compound. Some selected applications of these natural polymeric compounds are summarized in Table 1

Table 1 Application of natural polymeric substances as nanoinsecticides carrier

Polymeric carrier	**Active Substance**	**Functionality**	**Ref**
Diatomite-coated magnetic Chitosan	pH-responsively cypermethrin	High adhesion capacity on pests' epidermis, resulting in an improved efficiency against corn borers	Xiang et al. (2017)
hydrophilic methomyl	photocross-linkable carboxymethyl chitosan	Insecticidal activity of seven days against the armyworm larvae while the unformulated methomyl lasted only two days	Sun et al. (2014)
Sodium alginate nanocapsules	Pyridalyl nanocapsulated by leaf dipping method	Improved insecticidal potential against borer *(Helicoverpa armigera)*	Saini et al. (2014)
Sodium alginate nanocapsules	Imidacloprid	Improved insecticidal potential against leafhopper of okra, cytotoxicity of nanoparticles to Vero cells was lower than conventional formulation	Kumar et al. (2014)
Ethylcellulose nanocapsules	Emamectin benzoate	Improved insecticidal *potential Plutella xylostella* by leaf dipping method	Shoaib et al. (2018)
Ultrafine fiber of cellulose acetate	Avermectin via an electrospinning process	Continuous release of avermectin to achieve the insecticidal potential	Zhao et al. (2013)
Starch capsules with a diameter range of 0.7-4.8 μm	Avermectin by prexim membrane emulsification method	Avermectin contents of 16-47% offered a managed and delayed release of the insecticide of 14 days	Li et al. (2016)
Cassava starch	Nanosilver with 95-98% dichlorvos and chlorpyrifos	The enhanced surface area of silver nanodichlorvos and nanochlorpyrifos insecticides enabled the sustained release for 21 days	Ihegwuagu et al. (2016)
β-cyclodextrins and polycaprolactone (PCL)	Six neem oil	Offered insecticidal efficacy of eggs and nymphs *of Bemisia tabaci Gennadius*. The slow rupture of capsules restricted the betterment of insecticidal effect	Carvalho et al. (2012)

Synthetic Polymeric Substances

The biodegradable applications of synthetic polymeric materials in the pharmaceutical and cosmetic sectors motivated scientists to explore the possibilities of synthetic polymeric substances as nanocarriers in nano insecticides. These selected synthetic molecules are microbial degradable, biocompatible, and non-toxic, which gives a very safe impact on non-target organisms and the environment.

Polyethylene glycol (PEG) is available in linear or branched molecular chain structures with varying molecular weights. PEG is soluble in the majority of organic solvents and water. The United States Food and Drug Administration (USFDA) declared PEG safe to be used in medicines due to the absence of antigenicity and immunotoxicity, non-interference with conformations of polypeptides and enzymatic activities, as well as ease of excretion from living organisms. Polylactic acid (PLA) is the next synthetic polymer approved by USFDA to be used as a drug or cell carrier in the healthcare sector due to its modifiable biodegradable and mechanical behavior.

Polycaprolactone (PCL) is biodegradable polyester, continuously selected as a supervised delivery drug carrier and material for tissue engineering owing to its biocompatibility and miscibility with an extensive range of other polymers.

Polyhydroxy butyrate (PHB) is a biodegradable, biocompatible, and costly material that can be extracted from different renewable sources. The application of PHB as a nano carrier for insecticide is rarely published in scientific literature. Due to the miscibility and modification of these synthetic polymers, copolymers, inorganic carriers mixed polymers, and surface-modified function polymers are developed. Polymeric nano formulations have a remarkable potential for additional modifications and practical crop protection applications (Kah & Hofmann, 2014). Some selected applications of these synthetic substances are summarized in Table 2.

Table 2 Application of synthetic substances as nano insecticides carrier

Polymeric carrier	**Active Substance**	**Functionality**	**Ref**
PEG	Diethylphenylacetamide by phase inversion temperature emulsification	nano-formulated diethylphenylacetamide exerted better bioefficacy on the Japanese encephalitis vector *Culex tritaeniorhynchus*	Balaji et al. (2015)
PEG	Essential oil (EO) nanoparticles	Highly effective against mosquitoes *Culex pipiens*	Werdin et al. (2017)
PLA nanocapsules	lambda-cyhalothrin encapsulated by prexim membrane emulsification method	controlled delivery of lambda-cyhalothrin to give biocidal efficacy on Plutella xylostella	Liu et al. (2016)
PLA nanoparticles	Abamectin with different adhesive abilities to cucumber leaves	Sufficient biocidal efficacy on cucumber aphids	Yu et al. (2017)
PCL nanocapsules	*Rosmarinus officinalis L.* essential oil	Biocidal efficacy on red flour beetle *(Tribolium castaneum)*	Khoobdel et al. (2017)
PCL nanomicelles	polyethylene oxide PEO)	Enhanced the protection against *Tetranychus cinnabarinus*	Zhang et al. (2017)
PHB Nano-capsules	nanoformulations of neem (Azadirachta indica A.Juss)	Limited efficacy on armyworm larvae	Giongo et al. (2016)

Nanocomposites of UiO-66@ZnO/Biochar to embed carbendazim (CBZ) pesticide inside the three-dimensional structure for controlled application were produced to reduce the content of CBZ on plant leaves. The dimethyl sulfoxide (DMSO)-water mixture was used to prepare a spray solution of pesticide. The half-life time of CBZ@UiO-66@ZnO/Biochar by photodegradation rate was increased 12.3 times than free CBZ (Li Z et al., 2022).

Environmental Impact of Nano pesticides

Nano pesticides enter into the natural environment, after their field application and they may undergo a chemical transformation during their life cycle. The toxicity of nanopesticides depends on the attributes of nanocarriers and AcI. It was reported that in the presence of Cu $(OH)_2$ nano pesticide, degradation of thiacloprid is significantly slowed down which is a recalcitrant pesticide. Its prolonged persistence in soil could increase the risk of its action on nontarget organisms (Zhang, X., et al, 2019). Agricultural soils often contain a large number of organic pollutants of high human toxicity due to multiple applications of pesticides, and if the application of nano pesticides like $Cu(OH)_2$, impaired their degradation, this will raise major health concerns. Therefore more studies regarding the effects of nanopesticides on the fate of organic pollutants must be an active area of research, (Deng, R, et al; 2017) with the fabrication and application of various nanopesticides. This may reveal important information on environmental risk in terms of the effect of nanopesticide on the half-life of organic pollutants.

Nanopesticides also interfere with the normal metabolism of organisms as for example it was reported that Spinach showed significant changes in the metabolite profile when exposed to Cu (OH)2 nano pesticide, specifically nitrogen metabolism perturbation, which ultimately causes serious physiological issues for organisms (Zhao, L et al, 2017). The toxic effects of polymeric nanopesticides for plants and food have recorded little discussion.

Thus, studies related to different specific biochemical responses to nano pesticides are a critical area of research that will shed light on the impact of nano pesticides on environmental risks.

The polymer-based nano insecticides manufactured with liquid crystals, liposomes, and micelles are generally composed of natural phospholipids and cholesterol, which need surfactants' assistance, making pesticides toxic (Mustafa et al., 2020; Schnoor et al., 2018). Meredith et al. reported that the presence of the capsule may add to the toxic effect of lambda-cyhalothrin (LCT) a synthetic pyrethroid; while encapsulated Lambda-cyhalothrin- poses an acute toxicological effect to the different stages of zebrafish (Huang X, et al, 2022). The side effects of polymeric nano-pesticides are given in Table 3.

Table 3 Side effect of Nanopesticides on different plants

Nanopesticides and conditions	**Plant**	**Findings**	**Ref.**
$Cu(OH)_2$ nano wires 0.1050 and 1555 mg.L^{-1} for 30 days through foliar application	Lettuce (Lactuca sativa)	Triggered generation of ROS, which results in 23% decrease in the antioxidant capacity of lettuce leaves Caused unstable number of amino acids (e.g. 4-hydroxybutytic acid (GABA) decreased 50%)	(Zhao et al., 2016)
$Cu(OH)_2$ nano wires 4.8 mg cultivated for 45 days via foliar application	Low and high anthocyanin basil *(Ocimum basilicum)*	Increased the amount of fatty acids in low anthocyanin basil leaf Nanowires decreased the content of leaf fatty acids in high anthocyanin basil	(Tan et al., 2018)
$Cu(OH)_2$ Nanoparticles (Kocide 3000, DuPont) 0.100, and 1000 mg L^{-1} for 7 days via foliar application	Cucumber (Cucumis sativus)	accelerated N metabolism (e.g. arginine and proline amino acids metabolism).	(Zhao et al., 2018a)
Atrazine-loaded polymeric NPs, 2000 and 200 g ha^{-1} of atrazine via post- emergence foliar application	Slender amaranth *(Amaranth usviridis)* and hairy beggarticks (*Bidens pilosa*)	decreased photosystem II activity in both species . decreased root and shoot growth *in B. pilosa*	(Sousa et al., 2018)

Atrazine-loaded polymeric NPs 2000 and 200 g ha^{-1} of atrazine through post-emergence foliar application	Mustard (*Brassica juncea*)	Decreased photosynthesis, PSII quantum yield, shoot growth inhibition. Increased leaf lipid peroxidation.	(Oliveira et al., 2015a)
Copper nanoparticles	0, 200, 400, and 800 mg kg^{-1} for 60 days via foliar application	13 out 23 amino acids were up-regulated due CuNPs stress (e.g. tyrosine, increased up to 11 fold after exposure to 800 mg. kg^{-1})	(Huang et al., 2018b)
$Cu(OH)_2$ nanoparticles (Kocide 3000, DuPont)	Maize (*Zea mays*)	Decreased leaf photosynthetic pigment content (chlorophyll a and b). Reduced biomass by 17−20%.	(Zhao et al., 2018a)

Conclusion

It is expected to be able to improve pesticide efficacy, enhance AI stability, prolong its effective duration, and reduce environmental loads of pesticides. Recent research shows that several nanoparticles used in conventional nano pesticide formulations can be toxic to crops and beneficial organisms due to bioaccumulation and trophic transfer. Hence, it can be concluded that bio nanopestisides, containing AI and carrier molecules from biological sources are the most effective nanoinsecticides for pest management. It is eco-friendly and much more sustainable than others. It is essential to amplify the exploration of biogenic nanoparticles, and biopolymers and inventory them. The use of biogenic nanoparticles in agricultural land, demands further research and investigation. Based on the premise that the preparation of nanopesticides is stable and their quality is assured, there are not many technical barriers to their field application. The development prospects of nanopesticides are positive. The recent emerging trends in the engineered NPs include, the development of intelligent nanocarriers, RNA naopesticides, and the technology of unmanned aerial vehicles (UAVs) for plant protection has promoted the application of nanopesticides in the field.

References

1 Agostini, A.; Mondragón, L.; Coll, C.; Aznar, E.; Marcos, M.D.; Martínez-Máñez, R.; Sancenón, F.; Soto, J.; Pérez-Payá, E.; Amorós, P. 2012. Dual Enzyme-Triggered Controlled Release on Capped Nanometric Silica Mesoporous Supports. Chemistry Open, 1, 17–20.
2 Balaji A.P.B. et al., 2015. Nanoformulation of poly(ethylene glycol) polymerized organic insect repellent by PIT emulsification method and its application for Japanese encephalitis vector control. Colloids Surf., B, 128, 370- 378,
3 Campos E.V.R., de Oliveira J.L., Fraceto L.F. & Singh B., 2015. Polysaccharides as safer release systems for agrochemicals. Agron. Sustainable Dev., 35, 47-66
4 Carvalho S.S., Vendramim J.D., Pitta R.M. & Forim M.R., 2012. Efficiency of neem oil nanoformulations to Bemisia tabaci (GENN.) Biotype B (Hemiptera: Aleyrodidae). Semin. Cienc. Agrar., 33(1), 193-202
5 Deng, R.; Lin, D.; Zhu, L.; Majumdar, S.; White, J. C.; Gardea-Torresdey, J. L.; Xing, B. ;2017. Nanoparticle interactions with co-existing contaminants: Joint toxicity, bioaccumulation and risk. Nanotoxicology, 11, 591– 612, DOI: 10.1080/17435390.2017.1343404
6 Gebre SH, Sendeku MG. 2019. New frontiers in the biosynthesis of metal oxide nanoparticles and their environmental applications: an overview. SN Applied Sciences 1, 928.

7 He, B.C.; Chu, Y.; Yin, M.Z.; Müllen, K.; An, C.J.; Shen, J, 2013. Fluorescent nanoparticle delivered dsRNA toward genetic control of insect pests. Adv. Mater., 25, 4580–4584
8 Huang, Y. X.; Li, W. W.; Minakova, A. S.; Anumol, T.; and Keller, A. A.; 2018b. Quantitative analysis of changes in amino acids levels for cucumber (Cucumis sativus) exposed to nano copper. *Nanoimpact* 12:9-17
9 Ihegwuagu N.E. et al., 2016. Facile formulation of starch-silver-nanoparticle encapsulated dichlorvos and chlorpyrifos for enhanced insecticide delivery. New J. Chem., 40, 1777-1784
10 Kumar S. et al., 2014. Synthesis, characterization, and on field evaluation of pesticide-loaded sodium alginate nanoparticles. Carbohydr. Polym., 101, 1061-1067
11 Li D. et al., 2016. Preparation of uniform starch microcapsules by premix membrane emulsion for controlled release of avermectin. Carbohydr. Polym., 136, 341-349
12 Lowry G.V., Avellan A. & Gilbertson L.M., 2019. Opportunities and challenges for nanotechnology in the agri-tech revolution. Nat. Nanotechnol., 14, 517-522,
13 Li Z, Li Q, Jiang R, Qin Y, Luo Y, Li J, Kong W, Yang Z, Huang C, Qu X, Wang T, Cui L, Wang G, Yang S, Liu Z, Guo X., 2022. An electrochemical sensor based on a MOF/ZnO composite for the highly sensitive detection of Cu(ii) in river water samples. RSC Adv. Feb 10;12(9):5062-5071. doi: 10.1039/d1ra08376g. PMID: 35425559; PMCID: PMC8981263.
14 Meredith A. N.; Harper, B.; Harpe, S.L.; 2016. The influence of size on the toxicity of an encapsulated pesticide: a comparison of micron- and nano-sized capsules. Environ. Int. 86, 68-74.
15 Mustafa, I.F.; Hussein, M.Z.; 2020. Synthesis and technology of nanoemulsion-based pesticide formulation. Nanomaterials. 10, 1608
16 Nuruzzaman M., Rahman M.M., Liu Y. & Naidu R., 2016. Nanoencapsulation, nano-guard for pesticides: a new window for safe application. J. Agric. Food Chem., 64, 1447-1483
17 Oliveira, H. C.; Stolf-Moreira, R.; Martinez, C. B. R.; Grillo, R.; de Jesus, M. B.; and L. Fraceto, F.; 2015a. Nanoencapsulation Enhances the Post-Emergence Herbicidal Activity of Atrazine against Mustard Plants. *Plos One* 10 (7), 1-7.
Public Perception, edited by M. Rai and J. K. Biswas: Springer, 319-342
18 Saini P., Gopal M., Kumar R. & Srivastava C., 2014. Development of pyridalyl nanocapsule suspension for efficient management of tomato fruit and shoot borer (Helicoverpa armigera). J. Environ. Sci. Health, Part B, 49(5), 344-351
19 Schnoor, B.; Elhendawy, A.; Joseph, S.; Putman, M.; Chacón-Cerdas, R.; Flores-Mora, D.; Bravo-Moraga, F.; Gonzalez-Nilo, F.; Salvador-Morales, C. 2018, Engineering Atrazine Loaded Poly (lactic- co-glycolic Acid) Nanoparticles to Ameliorate Environmental Challenges. J. Agric. Food Chem. 66, 7889–7898
20 Shoaib A. et al., 2018. Preparation and characterization of emamectin benzoate nanoformulations based on colloidal delivery systems and use in controlling Plutella xylostella (L.) (Lepidoptera: Plutellidae). RSC Adv., 8, 15687-15697
21 Sousa, G. F. M.; Gomes, D. G.; Campos, E. V. R.; Oliveira, J. L.; Fraceto, L. F.; Stolloreira, R.; and Oliveira, H. C.; 2018. Post-Emergence Herbicidal Activity of Nanoatrazine Against Susceptible Weeds. *Frontiers in Environmental Science* 6.
22 Subramanian, K. S.; and Rajkishore, S. K.; 2019. Regulatory framework for nanomaterials in agri-food systems. In *Nanomaterials: Ecotoxicity, Safety, and*
23 Sun C. et al., 2014. Encapsulation and controlled release of hydrophilic pesticide in shell cross-linked nanocapsules containing aqueous core. Int. J. Pharm., 463, 108-114
24 Tan, W. J., Q.; Gao, C. Y.; Deng, Y.; Wang, W. Y.; Lee, J. A.; Hernandez-Viezcas, J. R.; Peralta-Videa, and Gardea-Torresdey, J. L.; 2018. Foliar Exposure of Cu(OH)(2) Nanopesticide to Basil (Ocimum basilicum): Variety-Dependent Copper Translocation and Biochemical Responses. *J of Agri.l and Food Chem.* 66 (13):3358-3366
25 Werdin J.O.G. et al., 2017. Polymer nanoparticles containing essential oils: new options for Mosquito control. Environ. Sci. Pollut. Res., 24, 17006-17015
26 Contreras-Cáceres, Rafael, Laura Cabeza, Gloria Perazzoli, Amelia Díaz, Juan Manuel López-Romero, Consolación Melguizo, and Jose Prados. 2019. "Electrospun Nanofibers: Recent Applications in Drug Delivery and Cancer Therapy" Nanomaterials 9, no. 4: 656. https://doi.org/10.3390/nano9040656
27 Xiang Y. et al., 2017. Fabrication of a controllable nanopesticide system with magnetic collectability. Chem. Eng. J., 328, 320-330

28 Yadav, R.K.; Singh, N.B.; Singh, A.; Yadav, V.; Bano, C.; Khare, S.; Niharika, 2020. Expanding the horizons of nanotechnology in agriculture: Recent advances, challenges and future perspectives. Vegetos, 33, 203–221.
29 Zhang, Colleen & Shen, Jie. (2022). Special Issue "Multifunction Nanoparticles and Nanopesticides in Agricultural Application" open for submission. 10.13140/RG.2.2.20776.65283.
30 Yu M. et al., 2017. Development of functionalized abamectin poly (lactic acid) nanoparticles with regulatable adhesion to enhance foliar retention. RSC Adv., 7, 11271-11280
31 Zhang, X.; Xu, Z.; Wu, M.; Qian, X.; Lin, D.; Zhang, H.; Tang, J.; Zeng, T.; Yao, W.; Filser, J.; Li, L.; Sharma, V. K.; **2019.** Potential environmental risks of nanopesticides: application of $Cu(OH)_2$ nanopesticides to soil mitigates the degradation of neonicotinoid thiacloprid. *Environ. Int.* , *129*, 42– 50, DOI: 10.1016/j.envint.2019.05.022
32 Zhao D., Zhang Y., Lv L. & Li J., 2013. Preparation and release of avermectin-loaded cellulose acetate ultrafine fibers. Polym. Eng. Sci., 53, 609-61
33 Zhao, L., Y.; Huang, C.; Hannah-Bick, A. N.; and . Keller A. A, 2016. Application of metabolomics to assess the impact of Cu(OH)(2) nanopesticide on the nutritional value of lettuce (Lactuca sativa): Enhanced Cu intake and reduced antioxidants. *Nanoimpact* ; 3-4:58-66
34 Zhao, L.; Huang, Y.; Adeleye, A. S.; Keller, A. A., **2017.** Metabolomics reveals $Cu(OH)_2$ nanopesticide-activated anti-oxidative pathways and decreased beneficial antioxidants in spinach leaves. *Environ. Sci. Technol.* , *51*, 10184– 10194, DOI: 10.1021/acs.est.7b02163