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A review on nanocomposites and their role in insecticide delivery

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Abstract

The extensive application of conventional chemical pesticides may result into several public health concerns as well as environmental hazards. To ensure food safety, use of alternative ecofriendly pesticide formulations is need of the hour. Nanocomposites, a special class of nanomaterials, having improved stability and barrier properties may be a viable option to develop environmentally benign slow/controlled release pesticide formulations. Presently, the use of nanocomposites in preparation of insecticidal formulations is in early stage of research and development. Application of different nanocomposite materials as vector for chemical insecticides have been summarized in this review with major emphasis on application arenas in crop protection, along with addressing limitations and prospects of this domain.

Keywords: ecofriendly, insecticides, nanocomposite, food safety

Introduction

Agrochemicals are inevitable agri-inputs from crop protection point of view. Annually around 30-40% crop loss occurs due to different pests, which makes the use of agrochemicals unavoidable. However, about 90% of the applied pesticides are lost into air or water bodies through drift hazards, run-off, or leaching^[1]. Indiscriminate use of these chemicals may also result into development of pesticide resistance in plants, residue problems, environmental pollution, loss of biodiversity and health hazards. To combat these problems, development of slow/controlled release formulations are important. These type of formulations can ensure targeted delivery in a sustainable manner which is both environmentally benign and economically feasible^[2].

Nanotechnology provides an alternative ecofriendly option to develop smart pesticide delivery systems. Nanotechnology has already been used in pest control, development of controlled release formulations, detection of agrochemicals etc.^[3, 4] The use of nanometric systems as vector for agrochemicals has different advantages such as improvement in efficiency due to higher surface area, higher systemic property due to advanced mobility, reduction in toxicity of residues due to abolition of organic solvents used in conventional pesticide formulations etc.^[5] Nanocomposites are one special type of polyphasic heterogeneous solid material having discontinuous reinforced phase in nano range (at least one dimension upto 100 nm) and continuous matrix phase^[6]. Use of nanocomposites has gained attention now-a-days due to their target specific delivery in case of controlled release formulations of nutrients and pesticides, wastewater decontamination and specificity in sensors for detecting pesticide residues. Use of nanocomposites as a tool for delivery of insecticides is in early stage of research. The present review aimed to develop a current state of art in application of these materials as insecticide delivery systems.

Importance of nanocomposites in crop protection

Nanocomposites have improved mechanical and thermal stability due to nano reinforced materials having high length/width ratio (aspect ratio) and specific surface area. This novel class of compounds have versatile applications in agricultural sector. Properties of nanocomposites are dependent primarily on properties of reinforcing phase and matrix used, and their interactions with each other^[7].

Different type of matrices/ carriers used for development of nanocomposites have been shown in fig 1. Polymeric nanocomposites provide major usage in development of controlled release (CR) formulations for crop production as well as crop protection. However, use of different materials such as Layered Double Hydroxides (LDHs), carbon nanotubes, carbon nanofibers, graphene oxides are also in

practise for development of nanocomposites useful for agricultural purposes. Development of nanocomposite based agrochemicals provides targeted and sustained delivery systems, thereby reducing chances of unwanted loss of agrochemicals in different environmental compartments, which in turn minimize probability of environmental risks and human health hazards.

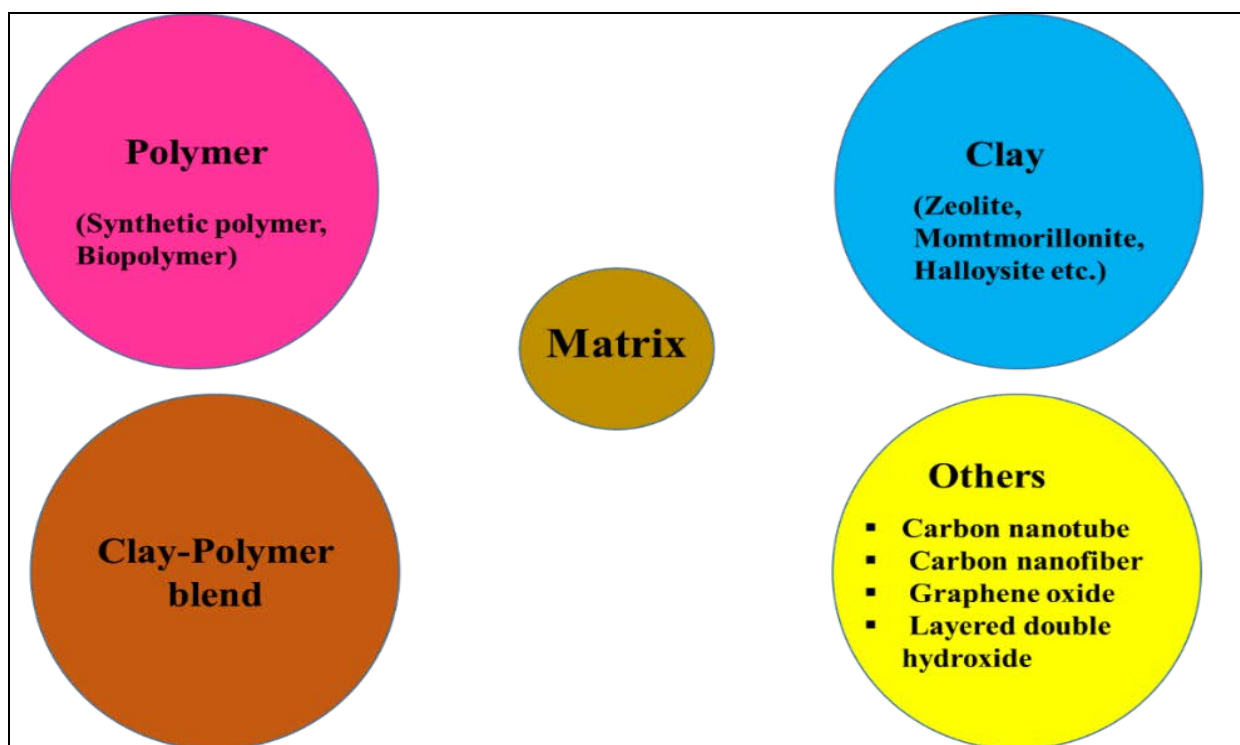


Fig 1: Matrices used for development of nanocomposites

Nanocomposite based insecticides

For effective and safe crop protection, the presence of active ingredients in minimum effective concentration within a formulation is a prerequisite. Nanocomposite based insecticidal formulations are important in this regard. Both natural and synthetic insecticide-based nano formulations using nanometric particles, nano capsules, nanofilms, etc. have been developed till date [8]. A novel photodegradable insecticide W/TiO₂/Avermectin nanocomposite was obtained by polyelectrolytes assembly, which prolonged the release time of the encapsulated avermectin microcrystals and higher toxicity against *Martianus dermestoides* in the adult stage as compared to control [9]. One chlorpyrifos nanocomposite had been developed by using bio-silica and straw-ash-based biochar, which showed a promising effect on reduction of losses through washing, volatilization, and leaching [10].

The use of biopolymer in the development of nanocomposite matrix is beneficial due to its low cost, biocompatibility, easy availability, and biodegradability. Enhanced pesticidal activity along with biocompatibility of chitosan nanocomposite has been observed [11]. This nanocomposite has been developed by using biocompatible polymer chitosan and insecticidal metabolites derived from fungal biopesticidal agent *Nomuraea rileyi*. Silver nanoparticles stabilized by cassava starch as the encapsulation matrix for dichlorvos and chlorpyrifos using a simple and cheap method has also been developed [12]. Release study of insecticides in water showed slow release of encapsulated insecticides and thereby proved potential of this approach in preparation of CR formulations of these insecticides. Alginate is another biopolymer which

can be used to develop controlled release insecticide formulations. However, some inherent properties like poor mechanical strength, excessive water uptake etc. are problems to exploit its potential in development of CR formulations. This problems can be eradicated by blending with clay or other polymers. Blending of alginate with ball-milled montmorillonite (MMT) clay modified by cetyl trimethyl ammonium bromide (CTAB) has developed alginate/exfoliated montmorillonite nanocomposites [13]. This material has been successfully used for loading of acetamiprid. The electrostatic interaction between the negative and positive charges of alginate COO⁻ groups and CTAB respectively had created 3D networks within the developed nanocomposite, which was helpful to improve the drug loading and encapsulation efficiency of the composite beads and also retarded the release rate of the test insecticide. Halloysite nanotube (HNT), a naturally occurring aluminosilicate, is also important in development of CR formulations. Nanocomposite film developed by incorporating deltamethrin loaded HNTs into low-density polyethylene based films has revealed controlled release behavior upto thirty two days [14]. Insecticidal activity of these films under greenhouse condition in alfalfa plants against aphids and thrips was also satisfactory.

Graphene oxide (GO), a 2D nanomaterial, is composed of carbon atoms with sp²-hybridization and prepared by oxidation of graphenes [15, 16, 17]. The properties of GO such as colloidal stability, water dispersibility, easy surface functionalization and biocompatibility render it as suitable nanocarriers for development of controlled release

formulations [18]. A novel GO nanocomposite has been developed for delivery of Pyridaben, chlorpyrifos and beta-cyfluthrin and their acaricidal activity has been tested against two spider mites, *Tetranychus truncatus* and *T. urticae* [19]. This study revealed the potential of GO in targeted delivery of insecticides along with having synergistic effect in control of spider mites. The synergistic mechanism was due to improvement in dispersibility and use efficiency of test pesticides adsorbed on the surface of spider mites. Similar observations were found in case of β -cyfluthrin, Monosultap and Imidacloprid, where GO synergized insecticidal potential of the test insecticides against a lepidopteran insect, Asian corn borer [20]. The synergistic action may involve physical damaging to the insect cement layer by GO, causing rapid water loss, disrupted cement layer may provide a new penetration points for insecticides, and GO-insecticide nanocomposite delivery system can enhance the insecticidal efficacy. Moreover, GO has also been used to modify polymer matrices to develop improved polymer based insecticidal formulations. One hydrophobic pesticide, Lambda-cyhalothrin was loaded on the temperature-sensitive polymer, Poly(N-isopropylacrylamide) modified by GO [21]. The developed formulation expressed improved water solubility, dispersion stability, photostability and biosecurity. Therefore, GO can be used to prepare intelligent pesticide formulations with the potential to improve the pesticide efficacy and has scopes in the practical application.

Layered double hydroxides are another important constituent for the development of nanocomposites. One approach was followed to develop an eco-friendly insecticide by using an ion-exchange method to intercalate a poor water-soluble insecticide, isoprocarb into zinc-layered hydroxide [22]. Recently, another simple and less time-consuming process of chitosan coating over Zinc hydroxide nitrate–Sodium Dodecylsulphate–Imidacloprid (ZHN–SDS–IC) nanocomposite has been developed for neutrally charged pesticides taking Imidacloprid as a test insecticide. The developed controlled release formulation has revealed the suitability of chitosan to be used as coating material and its potential to prolong the release of the intercalated Imidacloprid from the ZHN–SDS–IC nanocomposite [23].

Limitations and Future Opportunities

Nanocomposites have been found to be a potential alternative for delivery of insecticides. Regulatory framework is the major challenge in commercialization of nano-enabled products in agricultural sector. In India, department of biotechnology (DBT), Government of India has drafted the 'guidelines for evaluation of nano-agriinput products and nano-agriproducts in India' in 2019 to enhance the safety, quality and efficacy for commercialisation of nano-based agri-innovations [24, 25]. However, lack of uniform legislative framework throughout the globe is the major drawback for wide acceptance of nanotechnology based products including nanocomposites.

Uniform distribution and poor dispersion of nanofillers within the polymeric domain is another constraint of polymeric nanocomposites. Effect of shape, size and surface chemistry of nanofillers are also needed to be evaluated for augmenting the use of polymeric nanocomposites in crop protection. Biodegradability of nanocomposites, cost-ineffectiveness and difficulties in synthesis have also been identified as bottleneck for bulk use of these materials. Most of the experiments are confined into laboratory studies and/or pot experiments.

However, field evaluation is required for wide range acceptability in agricultural sector. Most importantly, limited studies have been done on environmental fate and ecotoxicity of nanocomposites. Therefore, future research works should be designed with focus on material chemistry, biodegradability, cost-effective simple synthesis techniques and environmental fate of nanocomposites for being potential alternative to conventional insecticide formulations.

Conclusion

Though agricultural productivity has been increased several fold due to application of agrochemicals, injudicious application of conventional agrochemicals have resulted into several human health hazards and environmental problems such as eutrophication, groundwater contamination, and toxicity to beneficial microorganisms etc. Therefore, use of nanocomposites as a delivery tool for pesticides is potent alternative for ensuring better food safety. The use of nanocomposites as vector for insecticides and their effects has been analyzed in this review. Future potential in exploitation of nanocomposite based insecticide formulations may become boon to crop protection sector provided further studies should be done on the present limitations pointed out in this article.

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