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Application of nanoparticles in determination of pesticides: A review.

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Abstract

Pesticides are mostly used to stop unwelcome pests from eating crops and livestock, which allowed them to enter the environment. Pesticide residues and their metabolites, which are present in the environment owing to overuse of pesticides, have a major negative impact on human health as well as the health of all other living things. The exposure to pesticides is linked to a number of serious illnesses (including cancer, chronic obstructive pulmonary disease, birth abnormalities, and infertility) as well as other harm to human health. There are many methods in which pesticides, which are frequently used in agriculture, might be transmitted to animals. As a result, accurate analytical techniques are needed to identify pesticide residues in environment. In this review the methods for quantifying pesticides using various nanoparticles (NPs) in human bodies, water, plant and soil have been determined.

Keywords: Pesticides, nanoparticles (NPs), pollution, environment.

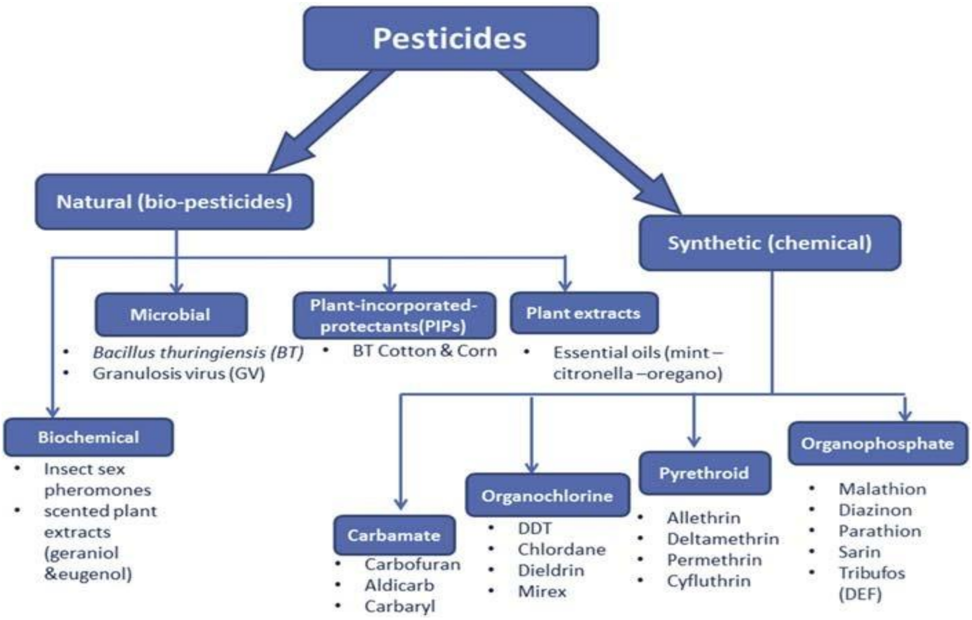
Introduction

Pesticides are compounds for eliminating and controlling any kind of pest, including insects and plants. Different kinds of pesticides have been widely employed in agriculture for high yield productions throughout the past few decades. Nearly one-third of global crop production is now protected by the use of pesticides. To meet the demands of an ever-growing human population, pesticides have improved food production. The large effects on pest management are advantageous for preventing dangerous diseases in agricultural crops (Nsibande & Forbes, 2016; Shim et al., 2023). The use of pesticides is also evident in non-agricultural settings, such as the maintenance of grass or the control of industrial vegetation (roadways, railroads). There is no way to prevent the widespread application of pesticides, which is constantly rising stay away from exposing them to the environment. To the extent of our worries, the rising trend in pesticide use is anticipated to continue for many years to come as human population rises and food need multiplies. In addition, the world is rapidly urbanising, which implies that less land will be available for farming, thus society must manufacture high yielding goods. Human health issues related to insect resistance and damage to the environment have been attributed to the strict pesticide usage. After repeated applications, pests will gradually acquire a resistance to the pesticides. In order to combat the numerous insect species, extensive research is done to find more powerful chemicals (Kamel & Hoppin, 2004). Pesticides can harm people in three different ways. First, the most significant source of exposure to these substances is through diet or ingestion. Second, it has benefited from home pesticide use through dermal contact. Finally, it might be caused by inhaling contaminated air, which could be a closely related exposure pathway, especially for people who live close to agricultural areas (Yusà, Coscollà, & Millet, 2014).

Pesticide use has significantly expanded, especially in agriculture, and as a result, they now provide numerous, high-quality crops at reasonable prices. However, if they are used excessively, they may release toxic residues into the soil, water, plants, and food, including metabolites and breakdown products. The presence of significant amounts of their residues in those intricate matrices has emerged as a major problem and may pose serious risks to human health and the environment. Therefore, it is urgently necessary to develop a device that can identify and break down these pesticides at the molecular and atomic level. One area that can be used for this is nanotechnology. The process entails working with atoms and molecules to create materials with nanometer-scale dimensions. In recent years, methods based on nanotechnology have gained international interest for the identification, breakdown, and elimination of dangerous pesticides. These methods are renowned for their great specificity in pesticide breakdown and detection (Shamsipur, Yazdanfar, & Ghambarian, 2016, Zhang and Fang, 2010).

Classification

Pesticides are mainly classified into two major group 1) chemical pesticides and 2) biopesticides. 1) Chemical pesticides are basically synthetic materials that directly kill or inactivate the pest. They are mainly classified as A) insecticides, B) herbicides, C) fungicides, D) rodenticide, E) nematicides. 2) Biopesticides are pesticides derived from natural sources like animals, plants, bacteria and certain minerals. For example, canola oil and baking soda have pesticidal applications and are considered biopesticides. Pesticides divided into four major families, namely as organochlorines, organophosphorus, carbamates and pyrethroids. The Aral Sea region is probably a typical illustration of how pesticide pollution affects human health. According to UNEP, "the range of oncological (cancer), haematological morbidity, and pulmonary dysfunction, in addition to immune system deficiencies and inborn deformities," are all affected by pesticides. When handling and/or treating pesticides to crops, farm workers run a very high risk of poisoning through skin contact and inhalation. There are two significant effects on human health from the breakdown of pesticide discharge in water. The first is eating fish and shellfish that have been exposed to pesticide contamination. Economic systems that rely on fish that reside at the bottom of the main agricultural submerged portions for survival may be threatened by this. The second is drinking pesticide-contaminated water directly. Organochlorines (OCs) pesticides are one of the most persistent chemicals that have high toxicity, lipophilicity and bioaccumulation. Moreover, OCs is found to be estrogenic, carcinogenic and resistance to environment degradation process. DDT (half-life of 3 to 20 years) is used in dealing with malaria disease as it control the population of mosquitoes. Carbamates are another class of pesticides which largely used in agriculture to protect crops against agriculture pests and household pests (Hassaan and Nemr, 2020; Firdoz et al., 2010).



Health effects

Pesticides cause several health effects such as endocrine disorders, effects on foetal developments, hepatic alterations and neurodevelopment disorders in children. Some psychological effects (anxiety, irritability, insomnia), some reproductive effects (birth effects, hostile uterus, preterm delivery), and some chronic neurotoxic effects (delayed organophosphate induced polyneuropathy, Alzheimer disease, attention deficit/hyperactivity disorder in children) (Vohra et al., 2020).

Chemistry for nanomaterials-based pesticides detection

There are two different types of chemistry for nanomaterials-based pesticides detection.

(i) **Homogenous chemistry:** In this procedure, the nanoparticles are first distributed throughout the pesticide-containing water sample. The pesticides in the water are detected by the distributed nanoparticles. Utilising all of the surface area that the nanoparticles present is a significant benefit of the process. However, once spread throughout the aquatic system, these nanoparticles are difficult to remove from the water. One potential disadvantage of this chemistry is that the distributed nanoparticles might contaminate the filtered water (Rawtani et al., 2018).

(ii) **Heterogeneous chemistry:** Before being employed for pesticide sensing, the nanoparticles are immobilised on various support materials in this procedure. These immobilised nanoparticle-containing support materials are applied to pesticide-contaminated water samples. The pesticide in the water is then found and broken down by the immobilised nanoparticles. One significant benefit of the procedure is that these support systems can be reused for other water samples. Another advantage of this strategy is that it prevents nanoparticles from clumping together when they are immobilised on solid supports (Rawtani et al., 2018).

Nanoparticles based approaches for pesticides detection

Nanoparticles (NPs) are nanoscale particles with sizes between 1 and 100 nm that are created using one of two methods: (a) top-down or (b) bottom-up. While the bottom-up method includes piling up the atoms and molecules of the bulk material to create nanoparticles, the top-down method entails breaking down bulk materials down to the nanoscale to produce NPs (Pandey et al., 2016). Unlike their bulk counterparts, these particles have distinct chemical, physical, and biological characteristics. These characteristics of NPs may be explained by their small size, distinctive form, and larger surface area. The three main types of nanoparticles (NPs) that have been employed by various studies to identify pesticides are metal, bimetallic, and metal oxide NPs.

(i) **Metal nanoparticles:** Numerous metal NPs, particularly noble metals like palladium (Pd), platinum (Pt), silver (Ag), and gold (Au), have found extensive use in the field of environmental remediation. In addition to these noble metal NPs, transition metal NPs such as iron (Fe), copper (Cu), and zinc (Zn) have been used. The advantages of NPs are their unique, rapid and delicate responses, simple production procedures, and low cost of reagents (Liu et al., 2008). As their size changes, gold nanoparticles (AuNPs) are known to display a variety of colours. AuNPs are the perfect optical material for detecting a variety of analytes because of their ability to change colour during different states of aggregation (Tsai et al., 2005). In the area of pesticide detection in various sources, particularly fruits and vegetables, AuNPs have found extensive use. The surface modification of these nanomaterials can improve their sensitivity and specificity towards various pesticides. A dipstick competitive immunoassay for the detection of dichlorodiphenyltrichloroethane (DDT) has been developed using AuNPs with detection limit (27ng/mL) (Lisa et al., 2009). Similar study has also been done to find kitazine in several food samples, including oranges, tomatoes, cucumbers, and grapes (Table 1) (Malarkodi et al., 2017).

Because of their distinct size and structure, silver nanoparticles (AgNPs) have a variety of electrical, optical, and magnetic properties. Because of these characteristics, AgNPs can now be used as antimicrobial agents, in a variety of fibre composites, and in biosensors (Rawtani et al., 2013). The optical characteristics possessed by AgNPs of different sizes have helped in the detection of numerous pesticides. AgNPs have been utilised to detect dipterex in various water samples after being capped with citrate. Because acetylcholinesterase's enzymatic function converts acetylthiocholine into thiocholine, citrate-capped AgNPs with immobilised acetylcholinesterase produced pink aggregates. Dipterex prevented thiocholine from forming because it hindered the enzymatic activity of acetylcholinesterase. As a result, the bright yellow AgNPs with their distinctive absorbance at 400 nm were able to stay free (Lia et al., 2014).

Table 1: Nanoprticles for Pesticides detection

Nanomaterial	Type of nanomterial	Pesticide	Detection limit	Reference
Metal Nanoparticle	AuNPs	DDT	27 ng/mL	Lisa et al., 2009
	AuNPs	Kitazine	0.65e2.44 mL/mL	Malarkodi et al., 2017
	AgNPs	Dipterex	0.18 ng/mL	Lia et al., 2014
Bimetallic Nanoparticle	Fe/Ni NPs	Profenofos	-	Mansouriieh et al., 2015
Metal oxide Nanoparticle	SiO2 NPs	Paraoxan	500 nM	Luckham and Brennan, 2010

(ii) **Bimetallic nanoparticles:** Atoms from two distinct metals combined into one nanoparticle are known as bimetallic nanoparticles. numerous researchers from all around the world have been interested in these NPs because of their numerous interesting and surprising properties that can be obtained by mixing two metals. The synergistic effects of the metals' combination result in the development of these novel properties in bimetallic NPs (Zaleska-Medynska et al., 2016). Fe/Ni bimetallic nanoparticles have been used to break down profenofos as a catalyst. The insecticide was broken down by nanoscale zero valent iron (nZVI) particles acting as a reducing agent. Ni aided in accelerating the rate of reaction and shielded the nZVI particles' surface from corrosion. During this study, the impact of three variables—pH, the quantity of Fe/Ni NPs, and the initial concentration of profenofos—on the degradation process was examined. At pH 5.12, with 1.4 mg/L of profenofos and 13.83 g/L of catalyst, the maximum removal rate (94.51%) was obtained (Mansouriieh et al., 2015).

(iii) **Metal oxide nanoparticles:** Environmental cleanup has made extensive use of metal oxide nanoparticles (NPs), mostly because of their superconducting qualities. These nanoparticles' superconducting properties give them a targeted and effective photocatalytic activity that has been used in many studies for pesticide detection and cleanup. Various metal oxide nanoparticles (NPs), such as iron oxide (Fe_2O_3 or Fe_3O_4 NPs), zinc oxide (ZnO NPs), titanium oxide (TiO_2 NPs), and silica (SiO_2 NPs), have been used to detect, break down, and remove pesticides from various sources. SiO_2 NPs have also been used in optical, electrochemical, SERS, or fluorescent techniques to detect pesticides. A "dipstick" colorimetric technique has been employed to detect paraoxan using AChE immobilised SiO_2 NPs. Along with the enzyme, AuNPs were also trapped in SiO_2 NPs to improve the pesticide's detection at extremely low concentrations (Luckham and Brennan, 2010).

Conclusion

Pesticides are frequently employed to manage and eradicate weeds and pest populations. Overuse of these agrochemicals has harmed avian habitat, decreased the number of insect pollinators, and threatened endangered species. They also caused many health issues. The several kinds of nanomaterials covered in this review have been used to detect pesticides from a variety of matrices, including water, fruits, and vegetables. Nanoparticles like AuNPs, AgNPs, and SiO_2 NPs, have been utilised to detect extremely low quantities of pesticides.

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