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Application of Nanochitosan in the Detection of Pesticide Residues and Degradation

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Abstract

Chemicals called pesticides are used to manage pests like weeds, rodents, and insects. They are commonly used in agriculture to safeguard animals and crops from pests and illnesses. The usage of pesticides, however, can potentially have detrimental effects on the environment and public health. Pesticides can harm non-target creatures and contaminate the soil, water, and air. In addition, exposure to pesticides can result in a variety of medical issues in people, such as cancer, neurological conditions, and reproductive issues. Chitosan is a natural polymer formed from crab shells. Nanochitosan is chitosan in a nanoscale form. It has several distinctive qualities that make it a potential material for a variety of applications, including the detection and degradation of pesticides, such as large surface area, biocompatibility, and non-toxicity. There are numerous ways to detect pesticides using nanochitosan. Utilizing sensors made of nanochitosan is one typical strategy. Usually, nanochitosan is immobilized onto a substrate, like a gold electrode, or nanochitosan-based colorimetric assays are used to create these sensors. Because there is currently no environmentally benign method of pesticide remediation, scientists have looked for other ways to prevent pesticides from having a negative impact on the ecosystem. In order to degrade pesticides, nanochitosan

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Charles Oluwaseun Adetunji, Maulin P. Shah, Yerima Mohammed Bello, Daniel Hefft, Jay Singh, Shyam S. Pandey and Ravindra Pratap Singh (eds.) Nanochitosan Applications for Enhanced Crop Production and Food Security, (383–408) © 2025 Scrivener Publishing LLC

has been used in a variety of ways. These include the usage of nanochitosan-based adsorbents, which are typically created by adding a functional group with a strong affinity for pesticides to nanochitosan. The pesticide is subsequently removed from the environment by the functional group after it attaches to it. Because nanochitosan can be impacted by environmental factors including pH and temperature, there are restrictions on its usage for bioremediation. Nanochitosan provides a number of benefits over other materials used for the detection and degradation of pesticides, notwithstanding its limits. As a result, it may be investigated to reduce the effects of pesticides on the environment.

***Keywords*:** Nanochitosan, pesticide, biodegradation, nanoremediation, chitosan

17.1 Introduction

Agriculture, which is constrained by a variety of biotic and abiotic factors, serves as the economic backbone of many developing countries because it generates both food and gross domestic product (GDP) [1]. However, with the enormous demand for food in line with the ever-increasing global population, there has been a rise in additional exploration to produce enough food with sustainable agriculture to satisfy consumers' current nutritional needs, increasing challenges like nutrient deficiencies, pest, soil erosion, water scarcity, and related diseases [2]. Pesticides and fertilizers have been used improperly and excessively to address pest-related issues, which has led to their classification as pollutants [3]. Moreover, the massive use of extremely harmful chemical pesticides, which have a negative impact on ecosystems and human health due to deposition, sorption with leaching tendencies that result in massive accumulation inside soil particles, biological molecules, and metabolic transmutation, is a major problem [3]. Furthermore, pesticide residues on produce have negative health effects [4]. A pesticide is a general term that refers to a large variety of synthetic and natural substances that are frequently used to manage pests. These substances include insecticides, fungicides, herbicides, plant growth regulators, and others. These include chloroacetanilides, organochlorines, organophosphorus, phenoxy derivatives, pyrethrins, pyrethroids, triazines, carbamates, dipyridyl derivatives, glycine derivatives, dithiocarbamates, benzimidazoles, and other unspecified substances [5].

Pathogens, insects, and weeds are responsible for crop losses of 13%, 14%, and 13%, respectively, according to a 2009 report. Herbicides account for 44% of all crop management chemicals used globally, followed by fungicides and bactericides (27%), insecticides (22%), and various other chemicals (7%) [6]. A pesticide should specifically be lethal to targeted pests and not non-targeted pests, although this declaration has brought up questions about the usage and misuse of pesticides. A pesticide, which is a rapid, simple, and affordable pest control option, has many uses in forestry, public health, and other areas of agriculture. In addition to their huge advantages, pesticides also pose threats to the ecosystem and unintended species when used [7]. Pesticides undergo chemical reactions including hydrolysis, photolysis, and biodegradation, which is collectively known as pesticide degradation [7]. This process results in the pesticide being converted into simpler components like water, carbon dioxide, and ammonia [8]. Both biotic transformation activities, which are mediated by microbes or plants, and abiotic transformation processes, such as chemical and photochemical reactions, are involved in the degradation of pesticides [8].

Adopting clever strategies to enhance soil quality and pest management with the introduction of new technology is urgently required. Nanotechnology has recently captured the interest and imagination of scientists and researchers due to recent advancements in the discipline [9]. With its quick development and unique applications, nanotechnology is finding new uses in the agricultural industry, particularly in the active ingredient delivery of nutrients, insecticides, and herbicides [10]. Chitin, a structural component found in multitudinous invertebrates and typically extracted from the exoskeletons of crustaceans, particularly shrimp and crabs, as well as fungi, yeast, and diatom cell walls, is converted into chitosan, a polycationic polymer [11]. It has historically been predominantly insoluble in water and several organic solvents due to its comparatively high hydrophobicity. Significant advancements have been made in the study and use of chitosan over the last 10 years. Chitosan is mostly employed in agriculture as a bio-pesticide, coating film, degradable mulch, food preservation, and plant growth regulator [12].

By alone, chitosan nanoparticles (ChNPs) have the potential to be powerful antibacterial agents and growth promoters for pathogenic fungi and bacteria [13]. Chitosan, with or without the combination of macronutrients, may function as a substituted sustained powerful biocide agent against crop pathogens such bacteria, fungi, and viruses in plant pathogen control and disease management [13]. Nanoparticle (NP)–mediated pesticide detection is a new technique that is gaining popularity in the agricultural sector. The stability, compatibility, and sensitivity of the NPs can be simply altered and range throughout a wide range. Pesticides are typically detected using NPs that are either grooved with fluorophores for surface-enhanced Raman spectroscopy or annexed with electrochemical, antibody, or enzyme-immobilized sensors [14].

This chapter elucidates the importance of chitosan in the detection of pesticides and their application for bioremediation purposes.

17.2 Pesticides and Their Chemical Nature

According to Nicolopoulou-Stamat *et al.* [15] and Hassan and Nemr [16], the term "pesticide" refers to a broad category of insecticides, fungicides, herbicides, garden chemicals, household disinfectants, and rodenticides that are used to both kill and protect against pests. The chemical and physical characteristics of these insecticides vary from one class to another. Because of this, it is admirable to classify them according to their characteristics and research their subgroups [16, 17].

Synthetic pesticides are manufactured from chemicals that do not naturally exist. Depending on their intended usage, they are divided into various groups. There are now three methods of classifying pesticides that are universally accepted [16]. These three often used methods of classifying pesticides include: (i) the chemical makeup of the pesticide; (ii) the mode of entry; and (iii) the activity of the pesticide and the species it kills [16]. According to their sources, chemical pesticides can be divided into four categories: carbamate, organophosphate, organochlorine, and pyrethroid pesticides [16]. The term "biopesticides" refers to a different type of pesticides that are naturally occurring or derived compounds, particularly from living creatures including plants, fungus, and bacteria [16, 17]. However, the classification, traits, and environmental effects of synthetic or chemical pesticides are the main emphasis of this review.

17.2.1 Classification of Synthetic Pesticides and Their Toxic Effect

The description of the active chemicals and the chemical makeup of the insecticides determine the most popular and acceptable technique for classifying them. It is a sort of classification that offers proof of the effectiveness, chemical composition, and physical characteristics of particular pesticides. Pesticides are divided into four primary groups based on their chemical makeup: organiochlorine, organic phosphorous, carbamate, pyrethrin, and pyrethroid (Figure 17.1) [16, 17].

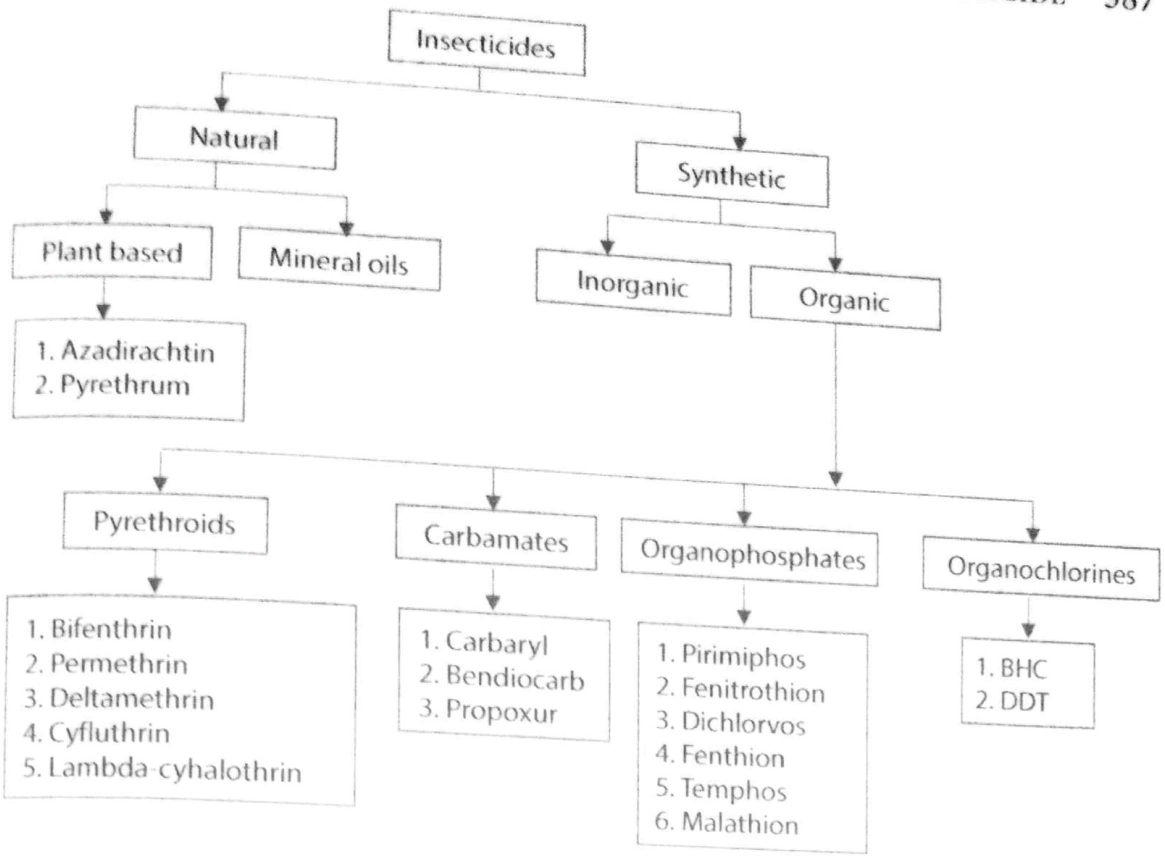

Figure 17.1 Classification of insecticides [16, 17].

17.2.1.1 *Pyrethroid Pesticides*

The chrysanthemum flower extracts known as pyrethrin, which are found in Kenya, are the source of pyrethroids, which are natural insecticides [16, 17]. By affecting the central nervous system, it alters the kinetics of sodium cation channels in nerve cell membranes, lengthening the time it takes for sodium channels to open. In both invertebrates and vertebrates, the sodium cation stream crosses the membrane [17, 18]. These effects may lead to a neuronal hyperexcitation [15, 16]. Scientists are now turning to the creation of synthetic pyrethroids due to the pressing need for huge quantities of these pesticides and the growing scarcity of essential oils required for the fabrication of natural organic pyrethrum [19]. The majority of pyrethroid insecticides share a number of traits, including being fast-acting, especially against chewing insects, low toxicity to birds and mammals, high toxicity to arthropods because it takes very small doses to kill insects, and highly toxic to fish if used directly on water [16, 17]. Despite the fact that many pyrethroid pesticides can be absorbed by insect pests when they walk on dry residues, they are ineffective at killing subsurface pests because of their strong adhesion to soil and organic substances. Additionally, according to

Nicolopoulou-Stamat *et al.* [15] and Hassaan and Nemr [16], they have poor water solubility. Even though there are more than 1,000 distinct pyrethroids in use today, only a handful are sold in the US. Many commercial goods, including pet shampoos, human lice treatments, pet sprays, topical mosquito repellents, and, of course, insecticide sprays for homes, businesses, and farms, contain pyrethroids as their active ingredient [15, 16].

17.2.1.2 *Carbamate Pesticides*

Herbicides, insecticides, nematicides, and fungicides, as well as several organic ester compounds produced from dimethyl N-methyl carbamic acid, are known as carbamates [5–18]. Cats and dogs both frequently utilize carbamates, including thiobencarb, propoxur, molinate, disulfiram (Antabuse), pyridostigmine, methiocarb, and carbaryl. The toxicity of carbamate compounds varies depending on their molecular makeup; however, they are generally less dangerous and last less time than organophosphates and organochlorines, the latter of which inhibit acetyl cholinesterase [15–18]. Acute carbamate poisoning is treated similarly to organophosphate toxicity. Given the transient nature of the carbamates, atropine administration should be done with greater caution. Organophosphate or carbamate insecticides frequently cause severe acute poisoning symptoms. The following is a list of the several organs where these poisoned symptoms can be seen: bronchial tree (dyspnea, coughing up more secretions, and muscarinic symptoms; cough, pulmonary edema, cyanosis, and bronchoconstriction), glandular stimulation (increased salivation, lacrimation, and sweating), cardiovascular effects (bradycardia, and hypotension), eye (miosis and blurred vision), bladder dysfunction (incontinence and frequency), gastrointestinal manifestations (nausea, vomiting, abdominal cramps, diarrhea, and incontinence), nicotinic receptor stimulation (including sympathetic and motor neurons), motor activity compromised (muscle twitching, depression of respiratory and circulatory, fasciculation, cramps, and weakness), sympathetic dysfunction (tachycardia, hypertension, and pallor), central nervous system effects (restlessness, emotional lability, confusion, drowsiness, Cheyne-Stokes respiration, slurred speech, tremor, ataxia, generalized weakness, coma, areflexia, convulsion, and hypothermia) [15–18].

17.2.1.3 *Organophosphate Pesticides*

Organophosphate insecticides are some esters made from phosphoric acid. Inhabitation of the enzyme acetylcholine, these esters form affects the human central nervous system [16–18]. Acetylcholinesterase is a neurotransmitter that disrupts nerve impulses by peacefully phosphorylating the OH group in the enzyme's active site, which is managed by this enzyme. The chemical structure of some pesticides is revealed by the intoxication symptoms of unconsciousness, nausea, headache, cramps, convulsions, and even death [16–18]. Atropine, which competes with acetylcholine at the muscarinic receptors, is the only effective treatment for organophosphate poisoning [16]. Up until the adult dose, the initial dose for adults is 2 to 5 mg IV or 0.05 mg/kg IV for children. Once the respiratory secretions have cleared and there is no bronchoconstriction, the dose is raised every 3 to 5 min if the patient does not respond to the treatment [16]. Hundreds of milligrams of atropine administered as a bolus or continuous infusion over the course of several days may be necessary in individuals with severe poisoning before they start to recover [16, 17].

17.2.1.4 *Organochlorine Pesticides (OCPs)*

Organochlorines are stable compounds that have the ability to build up in adipose tissue and are extremely persistent in the environment [16, 18]. These substances or their metabolites primarily affect the central nervous system in humans. This alteration of the enzymatic nerve membranes and electrophysiological properties results in altered K+ and Na+ flow kinetics through the nerve cell membrane, which may result in symptoms like acute poisoning death and seizures from breathing difficulty. Organochlorines can be divided into five groups based on their structural characteristics: (1) DDT and its analogs including DDT and dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD); (2) hexachlorocyclohexane (HCH), such as lindane; (3) cyclodienes including aldrin, dieldrin, endrin (sometimes referred to as "drins" in the literature), heptachlor, chlordane, and endosulfan; (4) toxaphene; and (5) mirex and chlordecone [16–18]. Some organochlorines, such as DDT, DDE, and DDD, have a 15-year field half-life, but aldrin and toxaphene have half-lives of 365 and 9 days, respectively. Death under natural conditions may be delayed and frequently viewed as a general wasting away or chronic sickness because the acute toxicity of the majority of OCPs typically occurs at doses that are greater than those thought to be environmentally realistic [16]. Most OCPs have a lipophilic, persistent character that might cause long-term storage in adipose tissue and release into the bloodstream under stressful environmental situations. Delays between the initial exposure and the onset of symptoms may result from this. According to several studies [15–18], DDT can linger in the body for up to 50 years.

The harmful effects of synthetic chemicals and their impacts on the ecosystem have made scientists seek out new technologies that are sustainable and eco-friendly in remediating the environment and alleviating the deleterious effects pesticides have on the ecosystem through the development and use of nanotechnology that utilizes chitosan in the environmental cleanup.

17.3 Properties of Chitosan Nanoparticles

Chitosan nanoparticles (ChNPs) are a form of nanomaterial that have a wide range of applications in a variety of industries, including the food, pharmaceutics, tissue engineering, agriculture, and medical fields [20].

17.3.1 Structure and Natural Origin of Chitin

Chitin is the second-most common natural polymer in the world after cellulose. Two marine crustaceans, including shrimp, crabs, lobster, and crawfish, are the main sources exploited and provide enough chitin/chitosan for the commercial sector [21]. D-glucosamine and N-acetyl-D-glucosamine are two subunits that make up the linear polymer chitosan, and they are connected by 1,4-glycosidic linkages [21]. The chitosan molecule's three rings make up its overall structure. It has three functional groups that make chemical modification simple, including amino groups, primary hydroxyl groups, and secondary hydroxyl groups [22]. These functional groups also affect the solubility and mechanical characteristics of chitosan. Additionally, chitosan has 1,4 glycosidic connections. Chitosan is more soluble than chitin in aqueous settings that are acidic. Chitosan is soluble primarily because of the protonation of -NH2 at the C-1 position of the D-glucosamine repeat unit, which, under acidic circumstances, converts the polysaccharide into a polyelectrolyte [23].

Chitosan can be used in almost all facets of human life and health, including agriculture, medicine, process engineering, and industries [24]. A number of fungi can be directly removed for their chitosan, but it can also be made by removing chitin and then deacetylating it. Chitin is a polymer that is produced by the zygomycetes, ascomycetes, basidiomycetes, deuteromycetes, and phycomycetes of the fungus kingdom more commonly than chitosan [25]. Chitosan, on the other hand, is only present in the cell walls of a small number of fungal taxa, mainly zygomycetes [25]. It is highly advantageous to extract chitosan from fungal biomass because it can be done whenever and is not affected by seasonal fluctuations. Chitin is only found in the cell walls of fungus, and it is extracted from them using the same procedure as is used to extract chitosan from crustaceans. Therefore, it is more cost-effective to use those fungi that already produce the desired output [25].

The exoskeletons of crustaceans, primarily a range of marine crustaceans including shrimp, crabs, and lobsters, are another crucial and abundant source of chitin. Currently, waste from the shrimp business serves as the primary source of chitin, with exoskeletons being used to extract both chitin and calcium. The chemical method of N-deacetylation is used to produce chitosan, and the free amino group left over after chitins' acetyl group was partially removed is what gives chitosan its cationic properties [26].

17.3.2 Chitosan Nanoparticles

Chitosan that has been altered to be smaller in size is known as nanochitosan; its size ranges from 100 nm to 400 nm [27]. It is possible to create ChNPs with the desired nanoscale properties, including a tiny size, specific surface and interface effects, and quantum size effects [27]. ChNPs have received a lot of interest recently for a variety of applications in the pharmacological, biological, and agricultural sectors [21].

17.3.2.1 Properties of Chitosan Nanoparticles

Numerous studies have demonstrated that the characteristics of chitosan NPs can range significantly depending on the processes employed for surface modification and preparation, which might result in applications in entirely different sectors [28]. For the past 10 years, chitosan has been studied as a potential material for shaping NPs. Making chitosan into NPs has improved its qualities. Chitosan NPs might exhibit typical activities because of the new properties of NP due to their small size and quantum estimation influence. They have a remarkable size and a large surface-to-volume ration and are simple, inexpensive, and easy to scale up. They are mucoadhesive and hydrophilic by nature, which increases their stability in the body and increases the security they provide to a typical tranquilizer. They fit a generic classification of drugs, tiny particles, proteins, and polynucleotides in this way. The benefits of typifying dynamic experts in a polymer framework include their regulated release and insurance from the surrounding medium or handling situations [29].

17.3.2.2 Synthesis of Chitosan Nanoparticles

Compared to the parent material, materials that have reached the nanoscale may exhibit enhanced or unexpected features. Numerous preparation methods (top-down, cross-linking, and microbiological) and potential application areas (electronics, textile, and medicine) for inorganic and organic NPs have been identified as a result of extensive research [28].

17.3.2.2.1 Emulsification and Cross-Linking Method

Chitosan NPs were originally prepared by emulsification and cross-linking using the amino group of the chitosan and the aldehyde group of a cross-linking agent. With the aid of toluene, glutaraldehyde, and Span 80 as stabilizers and cross-linkers, an emulsion composed of an aqueous chitosan solution and an oil phase is created [28]. After vigorous mixing of the phases, droplets that serve as the building blocks of the NPs are created. Centrifugation, numerous washing processes (with petroleum ether, acetone, sodium metabisulfite, and water), and vacuum- or freeze-drying are frequently used to separate NPs from the emulsion. Small-sized NPs with a restricted dispersion are attainable. However, because glutaraldehyde was found to have overt toxicity and difficulties with medication integrity, this approach is no longer in use [28].

17.3.2.2.2 Microemulsion Method

The reversed micelle (microemulsion) method is based on covalent cross-linking, just like emulsification and cross-linking, but it now uses water-in-oil reverse micelle structures to help produce ChNPs. Chitosan and glutaraldehyde from the aqueous phase are combined with an organic solvent and a lipophilic surfactant from the organic phase. Typically, n-hexane is favored as an organic solvent and cetyltrimethylammonium bromide or sodium bis (2-ethylhexyl) sulfosuccinate are employed as surfactants [28]. Chitosan NPs are created by cross-linking in a nanoreactor within the chitosan-containing micelle's core. The precipitation of surfactant with $CaCl_2$, dialysis to remove unreacted components, and freeze-drying are the three processes in the isolation of NPs. It is feasible to create ultrafine NPs with a size of less than 100 nm, which is a crucial characteristic for numerous applications where the particular surface area (loading capacity and sustained release) is crucial. Recently, the preparation process has been modified to use cross-linker and harmless solvents, which reduces the drawbacks of the traditional method based on glutaraldehyde [28].

17.3.2.2.3 Precipitation Method

Precipitation-based techniques can also be used to make ChNPs. Emulsification and precipitation are the foundations of the phase-inversion precipitation method [30]. A stabilizer (poloxamer), an organic phase (dichloromethane and acetone), and an aqueous solution of chitosan are used to create the oil-in-water emulsion [30]. To create well-dispersed emulsion droplets that are nanoscale in size, high-pressure homogenization is used. Then, acetone diffuses out of the droplets, and NPs precipitate simultaneously as methylene chloride is removed from the emulsion by evaporation at low pressure and room temperature [30]. As an alternative, there is the emulsion-droplet coalescence approach, which relies on the coalescence of two water-in-oil emulsions and causes the precipitation of NPs because NaOH acts as a precipitation agent in one of the emulsions. The two emulsions, one with chitosan and the other with NaOH, are created by first combining liquid paraffin and sorbitan sesquioleate. Using high-speed homogenization, an emulsion containing chitosan is created. When two emulsions are blended, NaOH diffuses into the ultrafine droplets, reducing the solubility of the chitosan and causing the precipitation of NPs. Three stages are required to produce NPs: centrifugation, washing with toluene, ethanol, or water, and freeze-drying [28]. Precipitation-method NPs are typically larger than 600–800 nm. The phase inversion precipitation method produces ChNPs with a high encapsulation efficiency for hydrophobic drugs like cyclosporin A, despite the fact that both methods are not particularly preferred due to the use of organic solvents and high energy requirements for homogenization applications [28].

17.3.2.2.4 Ionic Gelation Method

Ionic gelation is one of the most popular ways to create ChNPs, which have been studied for more than 20 years [31]. Its foundation is ionic cross-linking, which takes place when inversely charged groups are present. For instance, sodium tripolyphosphate (TPP) and the protonated amino groups of chitosan are negatively charged polyanion groups [32]. Aqueous TPP solution is added while being vigorously stirred after chitosan has been dissolved in an acidic aqueous solution (often an acetic acid solution). Chitosan molecules that are positively charged diffuse into one another, causing cross-linking that results in the production of NPs. Chitosan NPs can be produced using an oven method following a few centrifugations and water-washing procedures; drying, freezing, or drying [28]. It uses a simple method without solvents or hazardous cross-linkers. Additionally, the procedure may be completed at room temperature, and the size of the resulting NPs can be modified by varying the chitosan/TPP ratio, a significant characteristic that directly influences the effectiveness of drug encapsulation and delivery [28].

17.3.2.2.5 Top-Down Method

It is also possible to generate NPs via the top-down approach, which requires two steps: deacetylation (changing the acetyl group of the chitins with an amino group), and acid hydrolysis of the chitin to produce chitin NPs. Basically, a strong acid, like hydrochloric acid, is used to break glycosidic bonds, and the amorphous component is removed using a few centrifugation and washing processes. Chitin nanocrystals are isolated after several centrifugation steps. Chitosan NPs are chitin NPs that have been deacetylated to a degree greater than 60%. Unlike other techniques where drug loading occurs simultaneously with NP formation, this strategy requires a second loading step [28].

17.3.2.2.6 Green Synthesis Method

The creation of NPs utilizing microorganisms like bacteria, fungi, actinomycetes, and botanicals is known as "green synthesis." The bottom-up production of NPs is a method that integrates the fields of nanotechnology and biotechnology [33, 35]. The creation of NPs through biological means is preferred to chemical or physical means because it is a process that is safe, environmentally friendly, economically, and energetically viable; takes less time; and best utilizes the redox potential of metabolites produced by biological entities to transform macromolecules into nanoform [35]. According to Dutta *et al.* [35], the primary mechanism of biogenic production of the NP is based on redox reactions that take place when the microorganisms/biological entity binds to the metal ion and detoxifies it into the element metal through cellular enzymatic activity. Both internal and extracellular syntheses fall under this category. In intracellular synthesis, metal ions are brought inside the cell, where they undergo a reduction reaction in the cytoplasm, cell wall, and/or periplasm, leading to the formation of NPs inside the cell. But with the latter, the foreign object is trapped, and the reductase enzyme catalyzes the creation of NPs on the cell surface. Extracellular production of NPs is typically chosen since intracellular synthesis requires a laborious technique to harvest NPs from the cell matrix [35]. Due to their ability to produce NPs on a vast scale with a relative degree of control over their size and form (controlled by the surrounding environmental conditions) and a more straightforward production method, microorganisms are frequently characterized as environmentally benign, green nano-factories [35].

17.3.2.3 Characterization of Chitosan Nanoparticles

The processing environment and duration have a significant impact on NP production [35]. They are evaluated using the UV-vis spectrophotometer, electron microscope, dynamic light scattering, and Fourier transform infrared spectroscopy based on their surface plasmon resonance, morphology, particle size distribution, zeta potential, functional group analysis, etc. Additionally, atomic absorption spectroscopy is used to examine the release profile of NPs encapsulated in Ch [34, 36, 37].

17.3.2.3.1 Characterization by Dynamic Light Scattering

According to Sandhu *et al.* [38], the fundamental idea behind DLS is based on the Brownian movement of particles and molecules in a solution as a result of their interaction with randomly moving solvent particles. The photon detector measures the variation in scattered light caused by the random movement of particles after a laser beam has passed through the sample [34]. According to Karmakar *et al.* [39], DLS is used to quantify zeta potential, polydispersity index (PDI), and average particle size. The polydispersity or monodispersity of particles in an aqueous media is explained by PDI. A PDI number larger than 0.5 indicates polydispersity, and one less than 0.5 typically indicates monodispersity. Monodisperse ChNPs often have PDI values between 0.2 and 0.4 [40]. Additionally, the stability of the NPs, which is measured in the region of 30 mV, is explained by the surface charge of NPs, also known as zeta potential. Positive zeta potential measurements for the ChNPs range from 1.2–11.2 mV to 0.4–18.7 mV. Additionally, DLS's determination of the proper particle size revealed that the ChNPs are approximately spherical in form, with sizes ranging from 150 nm to 350 nm [28].

17.3.2.3.2 Characterization by UV-Vis Spectroscopy

The confirmatory investigation that establishes the creation of NPs via surface plasmon resonance is UV-vis spectroscopy. Using UV-vis absorption spectroscopy, the optical characteristics of ChNPs are investigated. ChNPs obtained from biogenic sources displayed the absorption band at 310–342 nm, in contrast to those obtained from the commercial manufacture of chitosan, which had an absorption band at 330.25 nm [34].

17.3.2.3.3 Characterization by Electron Microscopy

Transmission and scanning electron microscopes are used to examine the NPs' internal and exterior appearance [41]. According to transmission electron microscopy, ChNPs are frequently spherical in shape and amorphous in nature. Similar findings were made by other researchers using scanning electron microscopy, who discovered that the ChNPs have a nearly spherical form and a smooth exterior surface [41].

17.4 Application of Chitosan in Bioremediation of Pesticide

The agriculture industry's quick development has led to a significant increase in the amount of pesticides utilized. They must be removed since they pose a risk to others, which is why it is more important. Pesticides can be removed from contaminated water using chitosan derivatives. Following pseudo-first-order kinetics, Mostafa *et al.* [42] reported the removal of acephate, omthosate, and methyl parathion, three species of organophosphorus pesticides with adsorption capacities of 650.7 mg/g, 506.5 mg/g, and 560.8 mg/g, respectively. The pesticides adsorb to the adsorbate as monolayers, as evidenced by the data best fitted to Langmuir isotherm model. The composite demonstrated a promising activity in adsorbing the pesticides in the presence of inorganic anions such SO_4^{2}, PO_4^{3}, and NO_3, as well as the metal ions Zn^{2+}, Pb^{2+}, and Cd^{2+}. Adsorption was spontaneous, practical, and exothermic [42].

The SO_4^{2} had been reported to have a negligible impact, and other ions exhibited competitive behavior, which resulted in a sharp decline in the percentage of adsorption. For five trials, the chitosan/zeolite combination demonstrated stability in the removal of the organophosphorus insecticides [42]. It has been demonstrated that a magnetic chitosan/activated carbon bio-nanocomposite with a UiO-66 metal-organic framework is efficient at adsorbing the pesticide Imidacloprid, as well as CO^{2+} and the dye malachite green. The three contaminants mentioned above had adsorption capabilities of 25.2 mg/g, 44.5 mg/g, and 62.1 mg/g in ternary media, respectively. The data were well matched to the Langmuir isotherm model, and the pseudo-second-order kinetics of adsorption revealed that the adsorbates were adsorbed as monolayers through chemisorption. The created composite is a reusable, eco-friendly adsorbent that may be utilized to simultaneously remove several contaminants [40].

Chitosan has been used to remove pesticides from grape juice. According to Venkatachalapathy *et al.* [43], a 0.5% solution of chitosan removed 98% of chlorpyrifos and 97% of ethion in 1 h, and a 1% solution removed 96%, 95%, 94%, and 86% of phorate, fenthion, fenitrothion, and diazinon in 2 h. The effectiveness of flocculation/coagulation in removing pesticides from derivatives of chitosan that contain thymine has been reported in the past. The pesticides used are the Bordeaux mixture, Fastac 10 EC, and Karate Zeon, whose active pyrethroid constituents are alpha-Cypermethrin and lambda-Cyhalothrin, respectively; Novadim Progress, whose active organophosphoric ingredient is dimethoate; and Novadim Progress. Karate Zeon, Fastac 10EC, and Novadim Progress were all successfully removed by chitosan-thymine coordination, as well as 95% of the Bordeaux mixture. Charge neutralization caused the removal of Fastac 10 EC and Karate Zeon, whereas the combination of Novadim Progress and Bordeaux was eliminated by flocculation as a result of the combined action of charge neutralization, hydrogen bonding, and copper ion binding to the amine and thymine groups [44].

17.4.1 Nanochitosan in Pesticide Detection and Bioremediation

The significance of chitosan NPs in environmental remediation cannot be overemphasized owing to their unique properties and eco-friendliness. Below are the various ways in which nanochitosan functions in detection of pesticide in the environment.

17.4.2 Mechanism of Nanochitosan-Based Pesticide Detection

Due to its biocompatibility, biodegradability, antibacterial activity, and capacity to form NPs with different functional groups, nanochitosan has been employed as a material for the detection and degradation of pesticides. The type of sensor being utilized affects how nanochitosan-based pesticide detection works. Examples include the following:

17.4.2.1 Colorimetric Sensors

For the immobilization of enzymes or antibodies that can react with particular pesticides and cause a color change, these sensors use nanochitosan as a substrate [45]. For instance, acetylcholinesterase (AChE), an enzyme that is inhibited by pesticides containing organophosphorus and carbamates, was immobilized using nanochitosan. A spectrophotometer was able to measure a drop in the color intensity of the sensor as a result of the pesticides' inhibition of AChE [42].

17.4.2.2 *Fluorescence Sensors*

Fluorescent probes that can interact with pesticides and change their fluorescence properties are carried by nanochitosan in these sensors. For instance, quantum dots (QDs), which are nanoscale semiconductor crystals that generate fluorescence when stimulated by light, were enclosed in nanochitosan. Aptamers, which are short DNA or RNA sequences that may attach to particular targets, were used to functionalize the QDs. The aptamers were created to identify pesticides with an organophosphorus structure, such as chlorpyrifos and parathion-methyl. A fluorimeter was able to detect a dampening of the QDs' fluorescence as a result of the pesticides' binding to the aptamers [23].

17.4.2.3 *Electrochemical Sensors*

These sensors modify electrodes with nanochitosan so that the electrodes can produce electrical signals in reaction to pesticides. For example, gold electrodes that were further modified with graphene oxide (GO) and tyrosinase (TYR), an enzyme that can oxidize phenolic chemicals, were coated with nanochitosan [46]. By detecting the drop in current brought on by the herbicides' inhibition of TYR, the nanochitosan-GO-TYR electrode was able to identify phenylurea herbicides like diuron and linuron [46].

17.4.3 Bioremediation of Pesticides Using Chitosan Nanoparticles

Pesticides are being removed from the environment using a variety of ways. These include employing nanochitosan-based catalysts, adsorbents, and catalysts made of nanochitosan.

17.4.3.1 *Nanochitosan-Based Adsorbent*

Heavy metals, dyes, pesticides, medicines, and endocrine disruptors are just a few of the contaminants that can be removed from water using nanochitosan-based adsorbents [46]. The removal of pesticides from water can be accomplished using a variety of sustainable adsorbents, such as nanochitosan and its composites with other substances including graphene oxide, metal oxides, carbon nanotubes, and biochar [46]. In addition, the essay discusses the mechanisms of adsorption, kinetics, thermodynamics, and regeneration of the adsorbents. Singh and Saxena [47] conducted additional research to examine the possibility of nanotechnology in accelerating the bioremediation of pesticides from contaminated soil. The essay emphasizes how pesticide microbial breakdown is aided by nanomaterials like nanochitosan by improving their bioavailability, solubility, and mobility in the soil matrix [47]. An investigation on the adsorptive removal of three pesticides (atrazine, chlorpyrifos, and imidacloprid) from aqueous solutions using a chitosan/gelatin composite is presented in a research study by Attallah *et al.* [48]. The article assesses the effects of numerous factors on the adsorption process, including pH, contact time, initial concentration, and temperature. The article by Attallah *et al.* [48] also discusses the composite's adsorption isotherms, kinetics, thermodynamics, and desorption experiments.

17.4.3.2 Nanochitosan-Based Catalysts

Use of nanochitosan as a support or a modifier for other heterogeneous catalysts, such as metal oxides or metal sulfides, that may catalyze the oxidation and decomposition of pesticides under various conditions, is one strategy to improve the performance of nanochitosan for pesticide degradation. Based on the type of metal, the technique of synthesis, and the reaction mechanism, these nanochitosan-based catalysts can be divided into four groups: nanochitosan-metal NPs, nanochitosan-metal oxide composites, nanochitosan-metal sulfide composites, and nanochitosan-metal ion complexes are four examples of nanochitosan-metal materials [49].

Some examples of the application of nanochitosan in pesticide degradation using nanochitosan-based catalysts are as follows:

17.4.3.2.1 Nanochitosan-Copper Ion Complex

Nanochitosan was reacted with copper sulfate and sodium hydroxide to create this complex. Under the influence of visible light, the compound demonstrated catalytic activity for the breakdown of organophosphorus insecticides like malathion and dimethoate. The nanochitosan-copper ion complex, which could oxidize and break down the pesticides, was responsible for the degradation mechanism by producing reactive oxygen species (ROS) like hydroxyl radicals and superoxide anions [20].

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17.4.3.2.2 Nanochitosan-Titanium Dioxide Composite

The breakdown of organochlorine pesticides like DDT and endrin by this composite, which was made using the sol-gel process, was accelerated when exposed to UV light [49]. The composite increased the surface area and interaction between the photocatalyst and the pollutants by enhancing the dispersion and stability of titanium dioxide NPs on nanochitosan matrix [50]. Due to the pesticides' electrostatic attraction and hydrogen bonding with nanochitosan, the composite also demonstrated strong pesticide adsorption capacity.

17.4.3.2.3 Nanochitosan-Cadmium Sulfide Composite

With the aid of a microwave, this composite was created, and it demonstrated better photocatalytic activity for the breakdown of phenylurea herbicides like diuron and linuron when exposed to visible light [51]. By doping the cadmium sulfide NPs with nanochitosan, which decreased the band gap and increased conductivity, the composite improved the optical characteristics and charge transfer efficiency of the particles. The composite also shows excellent reusability and stability [51].

17.4.3.2.4 Nanochitosan-Gold Nanoparticle Composite

With the utilization of grape juice as a reducing agent, this composite was made utilizing a green technique [52, 53]. In the aqueous solution-based degradation of carbamate insecticides like carbaryl and carbofuran, the composite exhibited excellent catalytic activity. According to Amanulla *et al.* [53] and Hashem *et al.* [54], the degradation mechanism involves the catalytic reduction of carbamate pesticides by gold NPs supported on nanochitosan, which leads to the creation of less hazardous compounds.

17.4.3.3 Nanochitosan-Based Photocatalysts

Combining nanochitosan with other photocatalysts, such as metal oxides or metal sulfides, which can capture visible light and produce ROS that can oxidize and degrade the pesticides, is one way to improve the performance of nanochitosan for pesticide degradation [55]. On the basis of the elemental composition, band gap engineering, and charge carrier migration mechanism in composite photocatalysts, these nanochitosan-based photocatalysts may be divided into four groups: solid solutions, type II heterojunction nanocomposites, pure semiconductors, and Z-scheme [56].

17.4.4 Challenges and Limitations of Nanochitosan-Based Pesticide Detection and Degradation Technologies

The monitoring and repair of pesticide pollution in the environment can be accomplished using nanochitosan-based pesticide detection and degradation technology [57]. They do, however, also experience some difficulties and constraints that must be resolved. Among these are as follows:

For the synthesis, characterization, and assessment of nanochitosan and its derivatives for pesticide detection and degradation, there are no established procedures and protocols [58]. The reliability and repeatability of nanochitosan-based materials may be impacted by different approaches' potential for diverse attributes and performances [59]. The possible negative effects of using nanochitosan and its derivatives for pesticide detection and degradation on the environment and human health as they can potentially cause oxidative stress and even toxicity. Although nanochitosan is typically thought of as a biocompatible and biodegradable substance, its interactions with other nanomaterials, pesticides, or biological systems could change how hazardous and how it behaves. To ensure the safety and sustainability of nanochitosan and its derivatives, it is important to examine their fate, transport, accumulation, and transformation in the environment [59].

There are several obstacles encountered in the use of ChNPs among them is the incomplete understanding of the mechanism and kinetics of pesticide detection and degradation using nanochitosan. According to El-Naggar *et al.* [60], multiple physical, chemical, and biological mechanisms may be involved in the interaction of nanochitosan and its derivatives with pesticides. Further research is required to determine the factors, such as the type and concentration of the pesticide, the size and shape of the nanochitosan particles, the functionalization and modification of the nanochitosan, and the environmental conditions, that may affect the effectiveness and selectivity of the nanochitosan-based pesticide detection and degradation [61].

High prices and a limited supply of nanochitosan and its derivatives for pesticide detection and degradation are among the limitations on the use of ChNPs [62]. The natural resource chitin, which may be scarce and of poor quality, is the source of nanochitosan. Nanochitosan may need specialized tools, processes, and chemicals for its synthesis, purification, functionalization, and modification, which could raise the price and complexity of nanochitosan-based materials [62]. To make pesticide detection and degradation technologies based on nanochitosan more widely used and less expensive, they must be scaled up and commercialized.

17.5 Conclusion

A substance with great potential for pesticide detection and degradation is nanochitosan. It is superior to conventional approaches in a number of ways, including high sensitivity and selectivity, affordability and ease of access, non-toxicity and biodegradability, and adaptability (may be used for a variety of pesticides). Pesticides can be found using nanochitosan in a number of ways, such as colorimetric, fluorescence, and electrochemical sensors. Through the use of nanochitosan-based catalysts, adsorbents, and catalysts composed of nanochitosan, it has also been discovered that nanochitosan is efficient in the bioremediation of pesticide-polluted environments. In general, nanochitosan is a substance that shows promise for the detection and breakdown of pesticides. It differs from standard techniques in a number of ways, and it may be used to create new and improved pesticide detection and degrading technologies.

17.6 Future Perspective

A promising area of study that promises to lessen the negative effects of agrochemicals on the environment while also enhancing soil quality and crop yield is the employment of nanochitosan in the degradation of pesticides. A biopolymer called nanochitosan is created from the natural substance chitin, which is found in the exoskeletons of insects and crustaceans. In comparison to traditional chitosan, nanochitosan has various benefits, including a larger surface area, more reactivity, greater solubility, and lower toxicity. When combined with other nanomaterials like silicon, cellulose, or zinc oxide, nanochitosan can create nanocomposites with improved photocatalytic and pesticide adsorption capabilities. Future prospects for the use of nanochitosan in the breakdown of pesticides include the creation of innovative nanocomposites based on the substance that have increased efficacy, stability, and pesticide selectivity. The mechanisms and kinetics of pesticide degradation by nanocomposites based on nanochitosan under various environmental variables, such as pH, temperature, soil type, and others, must also be investigated. In order to maximize the effectiveness of the NPs, it is crucial to assess the environmental fate, toxicity, and breakdown products of nanochitosan-based nanocomposites in soil and water systems. For acceptance and widespread use for a better environment and the ecosystem as a whole, it is also essential to optimize the synthesis, characterization, and application methods of nanochitosan-based nanocomposites for large-scale manufacturing and field application. In order to evaluate nanocomposites based on nanochitosan as an alternative to conventional pesticides and remediation methods, it is also critical to consider their economic viability and social acceptability.

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