*polysaccharides*

*Review*

# Chitin- and Chitosan-Based Derivatives in Plant Protection against Biotic and Abiotic Stresses and in Recovery of Contaminated Soil and Water

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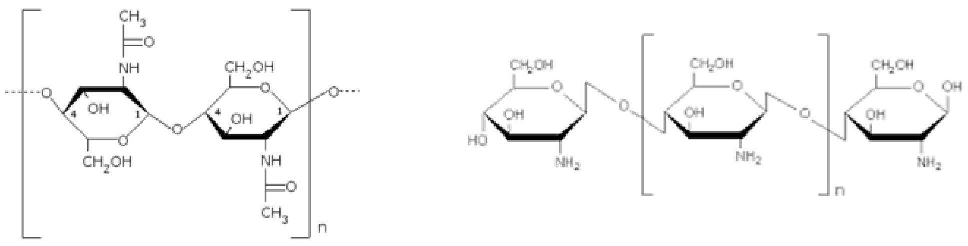
**Abstract:** Biotic, abiotic stresses and their unpredictable combinations severely reduce plant growth and crop yield worldwide. The different chemicals (pesticides, fertilizers, phytoregulators) so far used to enhance crop tolerance to multistress have a great environmental impact. In the search of more eco-friendly systems to manage plant stresses, chitin, a polysaccharide polymer composed of *N*-acetyl-D-glucosamine and D-glucosamine and its deacetylated derivative chitosan appear as promising tools to solve this problem. In fact, these molecules, easily obtainable from crustacean shells and from the cell wall of many fungi, are non-toxic, biodegradable, biocompatible and able to stimulate plant productivity and to protect crops against pathogens. In addition, chitin and chitosan can act as bioadsorbents for remediation of contaminated soil and water. In this review we summarize recent results obtained using chitin- and chitosan-based derivatives in plant protection against biotic and abiotic stresses and in recovery of contaminated soil and water.

**Keywords:** chitin; chitosan; defense responses; plant growth; recovery; stress

## 1. Introduction

Biotic (pathogen attack, herbivores, wounding), abiotic (deficient or excessive water, low or high temperature, high salinity, ultraviolet radiation, heavy metals, various toxic contaminants) stresses and in particular the unpredictable combination of different stresses are very harmful to plant growth and development, and lead to severe crop yield loss worldwide [1]. In consideration of the increasing food demand of the growing world population, it is becoming imperative to enhance crops' tolerance of multistress. So far, different approaches have been tested to increase plant resistance against stresses. In particular, an increasing resistance has been obtained by the use of different chemicals such as pesticides, fertilizers and phytoregulators. However, the extensive use of these chemicals in agriculture has a great environmental impact, with accumulation in soil, water and in living organisms [2]. This has stimulated the search of more eco-friendly mechanisms to manage plant stresses. Chitin, a naturally occurring long-chain high molecular weight polysaccharide composed of *N*-acetyl-D-glucosamine and D-glucosamine, a main component of the exoskeleton of arthropods and of the fungal cell wall, and its deacetylated derivative chitosan, seem promising tools to solve this problem (Figure 1).



Chitin Chitosan

**Figure 1.** Chemical structure of chitin and chitosan.

In fact, these molecules, easily obtainable from the crustacean shells of crabs, prawns etc., and are non-toxic, biodegradable and biocompatible. This accounts for their potentially broad application in agriculture where they can act as potent stimulators of plant productivity and protectors against pathogens ([3,4] and references therein]). In addition, chitin and chitosan can act as bioadsorbents for remediation of contaminated soil and water. The increasing industrial production and use of synthetic molecules such as dyes, pesticides, fertilizers, molecules containing heavy metal ions or nuclear residues are a major environmental concern. In fact, these compounds accumulate in soil and water and enter into food chains resulting in mutagenesis, carcinogenicity and other serious human health impairments [5]. To date, arrays of methodologies are in use to remediate this situation. Adsorption is the most attractive, in particular when it employs eco-friendly, sustainable, and low-cost materials such as chitin and chitosan [6].

After some pioneering indications in the early 1980′s on the protective effects of chitin and chitosan, an impressive number of papers dealing with the use of these molecules in an agricultural context have been published. These papers have been summarized in many exhaustive reviews ([2–4], among others]), thus in this review we summarize only recent results (years 2018–2020) obtained using chitin- and chitosan-based derivatives in plant protection against biotic and abiotic stresses and in recovery of contaminated soil and water.

## 2. Chitin- and Chitosan-Based Derivatives in Plant Protection against Biotic Stress

The total world population has increased from 2.5 billion in the 1950′s to over 7 billion in the present and is expected to increase to 9 billion by the end of the century. To feed this increasing population, food production must also rise, and in a safe and environmentally sustainable manner. At present, severe crop yield losses occur due to plant diseases and to global climate changes that have increased some phytosanitary emergences [7]. To fight these losses, several chemicals are still in use in modern agriculture. However, these agrochemicals are not without risk for the environment where their residues can easily accumulate. Thus, the implementation of novel strategies to manage plant disease is crucial to respond to the growing demand of safe and healthy food. In this perspective, chitin and chitosan are among the most promising tools. In fact, they can fight several stresses permitting relevant increases in plant productivity. The exact action mechanism of these protective molecules is under investigation and the different possibilities summarized in the following have been proposed (see [4] and references therein). Chitin and chitosan are positively charged molecules that can easily interact with the anionic structures present in the cell wall and in the cellular and nuclear membranes of pathogens like proteins, lipopolysaccharides and negatively charged ions. This can lead to leakage of intracellular components and the death of the microorganism. Interestingly, the negatively charged phosphate groups of nucleic acids can strongly interact with chitin and chitosan. This direct interaction can induce specific modifications in the expression and activity of proteins involved in the stress response. In addition, recent investigations strongly suggest the presence in the cellular plasma membrane of a specific receptor belonging to the glycoprotein family of lectins. The binding with this receptor starts a well-defined signaling cascade that leads to the responses. Finally, it should be noted that chitin and chitosan with their high nitrogen content and very low C/N ratio can directly act as natural fertilizers ([8] and references therein]). Whatever the mode of action, chitin, chitosan and their derivatives (e.g., nanoparticles (≤0.5 μm in size), microparticles (≥1 μm in size) and oligosaccharides, degradation products formed by no more than 12 glucosamine residues) permit a relevant increase in plant productivity by controlling several plant pathogens (Table 1).

**Table 1.** Chitin- and chitosan-based derivatives in plant protection against biotic stress.

| Plant Species | Characteristics of the Protective Molecules and Method of Administration | Protective Effect | Reference |
|---|---|---|---|
| *Capsicum annuum* L. | 1% chitosan, foliar application | Resistance against *Phytophthora capsici* | [9] |
| *Melissa officinalis* | 0.005, 0.01, 0.015% chitosan, shoot spraying | Accumulation of defense-related enzymes and phenolic compounds | [10] |
| *Phoenix dactylifera* L. | 0.1% chitosan nanoparticles, seedling irrigation | Enhancement of the innate immunity | [11] |
| *Solanum lycopersicum* | 0.001, 0.01, 0.1% chitosan microparticles, foliar application | Accumulation of defense-related enzymes | [12] |
| Stone fruit trees | 0.001% chitosan-Ag nanoparticles, foliar application | Resistance against *Pseudomonas syringae* | [13] |
| *Beta vulgaris* | 0.2% chitosan; 0.05% nano chitosan, foliar sprayjng | Resistance against *Pegomya hyoscyami* | [14] |
| *Solanum tuberosum* L. | 0.4% chitosan, tuber immersion | Resistance against *Fusarium* spp. | [15] |
| *Oryza sativa* L. | 0.3% chitosan oligosaccharide, seedlings sprayjng | Resistance against *Fusarium oxysporum* | [16] |
| *Citrus reticulata* Blanco | 0.05% chitin oligosaccharide, leaf infiltration | Resistance against *Candidatus* Liberibacter asiaticus | [17] |
| "in vitro" test | 0.5% chitin oligosaccharide diluted in culture medium | Inhibition of *Botrytis cinerea* spores germination | [18] |

Foliar application of chitosan enhances growth and modulates expression of defense genes in chilli pepper (*Capsicum annuum* L.) thus reducing the severe losses in chilli production induced by *Phytophthora capsici* infection [9]. Shoot cultures of *Melissa officinalis* treated with chitosan accumulate several defense-related enzymes and phenolic compounds with antimicrobial activity [10]. Similar results have been obtained in date palm (*Phoenix dactylifera* L.) seedlings treated with chitosan nanoparticles [11] and in tomato (*Solanum lycopersicum*) seedlings treated with chitosan microparticles [12]. A silver-chitosan nanocomposite reduces canker disease induced by *Pseudomonas syringae* pv. syringae in stone fruit trees [13] and chitosan and nano chitosan treatments efficiently control beet fly (*Pegomya hyoscyami*) infection in sugarbeet (*Beta vulgaris*) plants [14]. Similarly, chitosan alleviates diseases induced by *Fusarium* spp. in potato (*Solanum tuberosum* L.) [15] and by *Fusarium oxysporum* in rice (*Oryza sativa* L.) [16]. Interestingly, in Sun Chu Sha mandarin (*Citrus reticulata* Blanco) plants, hexaacetyl-chitohexaose, a chitin-derived oligosaccharide, affects the vitality of Asian citrus psyllid (*Diaphorina citri*), the hemipteran vector of *Candidatus* Liberibacter asiaticus, the pathogen associated with citrus greening disease [17]. In addition, efficacy of undiluted chitin-based cultures of *Paenibacillus elgii* HOA73 bacteria, a biocontrol agent that limits the damage caused to plants by microbial pathogens, insects, and nematodes, is comparable to that of standard chemical pesticides, suggesting a possible alternative to these chemicals in eco-friendly agriculture [18]. The suppressive effect of chitin added to the soil against pathogens often involves a change in the composition of the soil microbiota with an increase in the presence and activity of chitinolytic microorganisms that hydrolyze the chitinous hyphae of pathogenic fungi, and with an increase in secondary responders to added chitin that may affect pathogens [19]. However, it has been reported that deacetylation by specific enzymes of chitin oligomers converting them to ligand-inactive chitosan, is a strategy largely used by soil-borne fungal pathogens to prevent the protective effect of chitin [20]. These results indicate that more investigations are needed to exactly clarify the virulence strategy of soil-borne fungal pathogens.

## 3. Chitin- and Chitosan-Based Derivatives in Plant Protection against Abiotic Stress

To secure healthy and safe food of high nutritional quality to the growing world population and in particular, to consent adequate food access even in the present condition of global climate changes, it is necessary to increase plant resistance against abiotic stress too. In fact, abiotic stresses (temperature, water, salt, heavy metals, and UV radiation, among others) account for relevant losses in agricultural production worldwide [1]. To this end, in addition to selection of more performing crop genotypes, evaluation of new agronomic techniques and/or new agrochemicals without adverse ecological impact is needed. Water scarcity is regarded as the key restriction point for food production worldwide [21]. Thus, many investigations have been recently performed to ameliorate water utilization. Among the investigated substances, chitin and chitosan are able to confer tolerance to several abiotic stresses (Table 2).

**Table 2.** Chitin- and chitosan-based derivatives in plant protection against abiotic stress.

| Plant Species | Characteristics of the Protective Molecules and Methods of Administration | Protective Effect | Reference |
|---|---|---|---|
| *Zea mays* L. cv. White Pearl | 0, 2 and 4 g chitin added to 1 kg of soil | Drought stress tolerance | [22] |
| *Triticum aestivum* L. | 0.0125% chitosan, foliar application | Drought stress tolerance | [23] |
| *Triticum aestivum* cv. pishtaz | 0.0009% chitosan nanoparticles, soil and foliar application | Drought stress tolerance | [24] |
| *Zea mays* L. | 0.01% chitosan, foliar application | Drought stress tolerance | [25] |
| *Sesamum indicum* L. | 0.00048, 0.00064% chitosan, foliar application | Drought stress tolerance | [26] |
| *Origanum majorana* | 0.005, 0.02, 0.05% chitosan, plant irrigation | Drought stress tolerance | [27] |
| *Brassica napus* L. | 0.2% chitosan, seedling soaking | Drought stress tolerance | [28] |
| *Arabidopsis thaliana* | 0.01% chitin, plant spraying | Drought stress tolerance | [29] |
| *Triticum aestivum* L., *Zea mays* L. | 25, 50, 75% chitosan, seed coating | Salt stress tolerance | [30] |
| *Zea mays* cv. Arifiye | 0.1% chitosan, foliar application | Salt stress tolerance | [31] |
| *Solanum lycopersicum* Mill. | Chitosan–aggregated growth-promoting bacteria | Salt stress tolerance | [32] |
| *Zea mays* L. | 0.01% chitosan, seedling soaking | Cadmium stress tolerance | [33] |
| *Solanum melongena* L. | 0.0125, 0.0150, 0.02% chitosan, foliar application | Heat stress tolerance | [34] |
| *Capsicum annuum* L. | 0.00125, 0.00250, 0.00375% chitosan, plant spraying | Heat stress tolerance | [35] |
| *Solanum lycopersicum* Mill. | 0.003, 0.006, 0.009, 0.012% chitosan, foliar application | Heat stress tolerance | [36] |
| *Solanum tuberosum* L. | 0.25, 0.5% chitosan, foliar application | Poor soil tolerance | [37] |
| *Phaseolus vulgaris* cv. Contender | 10% chitosan nanoparticles loaded with NPK fertilizers, seed priming and foliar application | Poor soil tolerance | [38] |
| *Mokara* Orchids Hybrids | 0.002, 0.004, 0.008% chitosan, foliar application | Poor fertilization tolerance | [39] |
| *Solanum lycopersicum* | 1 mg/plant of chitosan, applied to the soil in the transplant cavity | Poor fertilization tolerance | [40] |
| *Fragaria* x *ananassa* Duch. cv. Elsanta | 0.001% chitosan, foliar application | Poor fertilization tolerance | [41] |

For example, chitin added to the soil at the beginning of the experiment induces water-stress tolerance in maize (*Zea mays* L.) plants grown under regulated deficit irrigation [22]. Chitosan application has the potential to mitigate the water deficit effects on yield and quality of wheat (*Triticum aestivum* L.) [23], and in the same plant species chitosan nanoparticles decrease the adverse effects of drought stress [24]. Similarly, leaf application of chitosan renders maize (*Zea mays* L.) hybrids more tolerant to water stress [25] and decreases the plant damage under drought stress in sesame (*Sesamum indicum* L.) [26]. Chitosan furnished as water solution alleviates water stress in marjoram (*Origanum majorana* L.) [27], and application of chitosan solution during sowing increases resistance against drought stress and the amount of oil in rape (*Brassica napus* L.) [28]. Basic studies conducted in the model plant *Arabidopsis thaliana* suggest that chitin modulates water balance through its action on vascular bundle sheath and mesophyll cells [29]. About other stresses, chitosan application alleviates salt stress thus improving growth performance in *Triticum aestivum* L. and *Zea mays* L. [30], and confers tolerance to salt stress in maize seedlings by enhancing the expression and activation of alternative oxidase [31]. Interestingly, inoculation of chitosan-immobilized plant growth-promoting bacteria improves growth of tomato plant (*Solanum lycopersicum* Mill.) under salt stress conditions suggesting the use of this eco-friendly and sustainable approach to fight salt stress [32]. Finally, chitin and chitosan use permits the cultivation of crops even in non-optimal conditions and the conservation of energy and other resources. For example, chitosan treatment alleviates cadmium stress in maize (*Zea mays* L.) seedlings, permitting their growth in areas subject to heavy metal stress [33] and application of chitosan protects eggplants in field (*Solanum melongena* L.) against heat and high irradiance stresses [34]. Chitosan spraying on sweet pepper plants (*Capsicum annuum* L.) permits their growth in unheated greenhouse conditions [35]. Similarly, foliar application of chitosan or chitosan nanoparticles has positive effects on different plant species. In fact, it ameliorates growth and the quality of tomato (*Solanum lycopersicum* Mill.) plants under plastic tunnel conditions [36]. It also stimulates tuber yields of potato (*Solanum tuberosum* L.) plants grown under newly reclaimed sandy soil conditions [37]. Finally, when supplemented as nanoparticles loaded with an NPK fertilizer, it ameliorates growth and productivity of French bean (*Phaseolus vulgaris* cv. Contender) plants grown in clay–sandy soil [38]. Last but not least, chitin and chitosan treatments permit relevant savings in the use of very expensive and high ecological impacting chemical fertilizers and cultivation in soil with limited nutrients. Chitosan ameliorates inflorescence quality and commercial half-life of *Mokara* orchid hybrids grown at half the regular application fertilizer dosage [39]. Chitosan stimulates growth of tomato (*Solanum lycopersicum*) plants [40] in poor soil conditions, and it promotes growth, fruit yield and quality in strawberry plants (*Fragaria* x *ananassa* Duch.) cv. Elsanta grown under nutrient limitations [41].

Chitin and chitosan can protect plants against abiotic stress with different mechanism with respect to different stresses. For example, their foliar application induces drought tolerance by direct antitranspirant coating, induction of stomatal closure, accumulation of stress protective enzymes and metabolites ([42] and references therein]). Similarly, chitin and chitosan can affect heat stress by abscissic acid accumulation, which is linked with the previous reported induction of stomatal closure ([42] and references therein]). Salinity stress is relieved by accumulation of antioxidant enzymes and reduction of lipid peroxidation ([42] and references therein]). Finally, due to the presence of functional amino and hydroxyl groups, chitin and chitosan are also able to form complexes with several heavy metals, thus reducing their bioavailability and alleviating their phytotoxicity ([42] and references therein]).

## 4. Chitin- and Chitosan-Based Derivatives in Recovery of Contaminated Soil and Water

Accumulation in the environment of heavy metals and other pollutants released from various human activities is increasingly becoming a very serious problem. In fact, these compounds are highly toxic, mutagenic and carcinogenic even at low concentrations. In addition, most of them are non-biodegradable. Thus, the development of efficient methods for their removal from the environment is an imperative goal and from this perspective, bioadsorption is recognized as an economic and effective option [6]. Furthermore, an efficient elimination of contaminants allows the reuse of increasingly rare and precious resources such as fresh water and cultivable soil. For their low cost of production, biocompatible and biodegradable nature, high resistance to mechanical and antimicrobial attack with a consequent lack of generation of potentially hazardous secondary end products, the use in these areas of chitin- and chitosan-based adsorbents is widely tested [6]. In addition, the chemical structures of chitin and chitosan easily allow their integration with specific ions, molecules and materials to obtain complex structures for selected applications such as those described in detail in the papers summarized in Table 3.

**Table 3.** Chitin- and chitosan-based derivatives in recovery of contaminated soil and water.

| Contaminated Environment | Characteristics of the Protective Molecules | Contaminant(s) | Reference |
|---|---|---|---|
| "In vitro" assays | Iron/chitin nanoparticles | Heavy metals, dyes, microorganisms | [43] |
| Soil and water | Carboxylated graphene oxide/chitosan/cellulose nanocomposite | Copper ions | [44] |
| Soil, water and seedlings | Carboxylated graphene oxide/chitosan/cellulose nanocomposite | Copper ions | [45] |
| Water | Chitosan/polyvinyl alcohol/montmorillonite clay membrane | Chromium ions | [46] |
| Soil | Chitosan/Prussian blue microgel | Cesium and other radionuclides | [47] |
| Soil | Chitosan nanoparticles | Lead and copper ions | [48] |
| Water | Chitosan microspheres | Copper ions | [49] |
| Water | Chitosan/packed columns | Arsenic ions | [50] |
| Water | Hyacinth plant extract/chitosan nanocomposite | Copper, lead and cadmium ions | [51] |
| Water | Chitosan/*Lemna gibba* hybrid system | Boron ions | [52] |
| Water | Chitosan/laccase/arginate matrix | 17$\alpha$-ethinylestradiol | [53] |
| Water | Chitosan/mesoporous carbon material | Tetracycline antibiotics | [54] |
| Soil and water | Chitin- and chitosan-containing mushroom stem waste | Paracetamol, 17$\alpha$-ethinylestradiol | [55] |

**Table 3.** *Cont.*

| Contaminated Environment | Characteristics of the Protective Molecules | Contaminant(s) | Reference |
|---|---|---|---|
| Water | Chitosan/*Serratia* sp. W4-01 carbon beads | Diesel oil | [56] |
| Soil and water | Chitosan/*Serratia* sp. AC-11 carbon beads | Polycyclic aromatic hydrocarbons | [57] |
| Water | Chitosan/zero-valent iron nanocomposite material | Trichloroethylene | [58] |
| Soil | Chitin-rich crustaceans shells | Hexahydro-1,3,5-trinitro-1,3,5-triazine; 2,4-dinitrotoluene | [59] |
| Water | Chitosan beads and cells of *Arundo donax* L. plants | CI Basic Red 14 dye | [60] |
| Water | Chitosan-lignin-titania nanocomposite | Brilliant Black dye | [61] |
| Soil and water | Chitosan nanoparticles | Paraquat | [62] |
| Soil and water | Chitosan formulations | Glyphosate | [63] |
| Water | Chitosan and electroless nickel plating | $CO_2$, $SO_2$ | [64] |

As far as heavy metal removal is concerned, iron/chitin nanoparticles were successfully tested "in vitro" for antimicrobial and environmental applications [43]. Carboxylated graphene oxide/chitosan/cellulose composite beads efficiently remove $Cu^{2+}$ from water and soil [44] and reduce its bioaccumulation in wheat plants [45]. Novel chitosan-based nanomembranes can be used to treat industrial wastewater contaminated by chromium [46] and chitosan-based magnetic microgels for the cleaning of cesium-contaminated clay [47]. Nano-fungal chitosan removes $Pb^{2+}$ and $Cu^{2+}$ from the water and soil matrix [48], while microfluidically-generated chitosan microspheres adsorb Cu ions from industrial wastewater [49]. Sorption studies carried out on contaminated groundwater using columns packed with chitosan demonstrate the capability of these columns to remove arsenic compounds [50]. Interestingly, a composite of chitosan/water hyacinth plant (*Eichhornia crasspes*) has an excellent absorption of Cu, Pb, and Cd ions [51] and an unconventional method based on chitosan adsorption and duckweed (*Lemna gibba* L.) phytoremediation efficiently removes boron from freshwater reservoirs [52], suggesting that these integrated methods can be very useful in wastewater treatment. Many pharmaceutical agents can be also removed from the environment by chitin- and chitosan-based derivatives. For example, a matrix based on laccase–alginate–chitosan efficiently removes, from aquatic environments, 17$\alpha$-ethinylestradiol, the synthetic estrogen widely used in oral contraceptives and in hormonal replacement therapy that the conventional water treatment processes are unable to completely eliminate [53], while mesoporous carbon materials prepared with chitosan as pore-forming additives adsorb tetracycline antibiotics [54]. Very interestingly, chitin and chitosan-containing mushroom stem waste can be directly used for adsorption of pharmaceutical products like paracetamol and 17 $\alpha$-ethynyl estradiol present in soil and surface water, reducing costs and environmental impacts [55]. Similarly, chitin and chitosan containing materials, often in combination with microorganisms and plants, can be used to contrast hydrocarbons and synthetic dye contamination that more and more frequently occurs in the environment as a result of human activities. For example, bacteria of *Serratia* sp. W4-01 strain immobilized in chitosan-activated carbon beads can remove diesel oil from contaminated water [56], while bacteria of *Serratia* sp. AC-11 strain immobilized in similar beads can degrade polycyclic aromatic hydrocarbons [57] more efficiently than the free-living cells. Interestingly, a novel amphiphilic nanocomposite material covered by chitosan can degrade trichloroethylene [58], suggesting a possible use of this approach for air decontamination, too, and addition of chitin-rich crustacean shells to soil can positively affect microbial and fungal communities, helping biodegradation of aromatic compounds [59]. Beads formed by chitosan and cells of *Arundo donax* L. plants can be used as an effective adsorbent for CI Basic Red 14 dye from water [60], while chitosan-lignin-titania nanocomposites can efficiently remove Brilliant Black dye from aqueous solution [61]. Chitin and chitosan formulations can also be used as a carrier to maximize herbicide activity thus reducing their dangerous accumulation in the environment. For example, paraquat loaded into chitosan nanoparticles shows enhanced herbicide activity accompanied by decreased soil penetration, cytotoxicity and mutagenicity [62] and chitosan/glyphosate formulations show less phytotoxicity and better herbicidal activity than the commonly used salt form of glyphosate [63]. Finally, chitosan supplementation can help to reduce the environmental impact in terms of greenhouse gas emissions and soil acidification of industrial wastewater treatments with respect to the existing chemical treatment process [64].

## 5. Open Questions, Future Perspectives and Conclusions

The impressive number of papers published in recent years dealing with the use of derivatives based on chitin and chitosan in plant protection against biotic and abiotic stresses and in remediation of contaminated soil and water attests to the relevance of these themes. In fact, the huge environmental impact of human activities needs to be faced with new more eco-friendly but cost-effective approaches. Chitin and chitosan are abundant, cheap, and environmentally friendly molecules. In fact, chitin is the second large renewable carbon source in the world after cellulose and its production from seafood industry waste amounts to over $10^{11}$ tons per year. Chitin can be easily and with low cost transformed into chitosan by treatment with NaOH even though this industrial method of preparation produces not a unique compound but many polymers differing in deacetylation and polymerization degrees, viscosity and molecular mass. Although this can negatively affect the final cost of production, the purification and characterization of these industrial products to ensure reproducible effects should be a very important goal. In its absence, it should be noted that the term "chitosan" cannot be considered univocal and to obtain reproducible results it is very important to specify the lot of production of the chemical. In fact, the above reported chemical differences can greatly affect the biological properties of the compound ([3] and references therein]). On the other hand chitin and chitosan can be easily degraded by specific and unspecific enzymes produced by different microorganisms present in the soil and their degradation products are not toxic to humans ([65] and references therein]). Thus, their utilization as biostimulants of stress responses and bioremediation agents will be more and more relevant. This is evidenced by the growing proposal of industrial products based on chitin and chitosan, for example CHITOSAN 6 from Rumexo Ltd. (Derby, UK); Chitosan Clorohydrate from Agrilaete (Udine, Italy); Chitosan Biorend from Tekcnofarm (Caserta, Italy). The utilization of chitin and chitosan preparations in agriculture has been normed at European level and authorized for use in organic farming [66]. However, it must not be forgotten that up to now most of the studies on the effects of these preparations are at the laboratory or greenhouse level and extensive field experiments are still lacking. This is very important when chitin and chitosan are complexed with other molecules in particular metals. Potential effects of these derivatives on the environment must be considered. Reports on the toxicity of these metal-complexed derivatives on the ecosystems and humans are contradictory and strongly suggest further study to eliminate the possibility of serious impacts on living organisms ([3] and references therein]). In any case, despite the still open questions, chitin- and chitosan-based derivatives have proved useful in many aspect of agricultural practices as well as in remediation of contaminated soil and water and appear to be very interesting tools for the development of more sustainable food production and environment conservation practices.

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