Chitosan in Agricultural Context-A Review

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ABSTRACT
Chitosan is a poly (1, 4)-2-amino-2-deoxy-β-D glucose, a de-acetylation product of chitin, found in exoskeleton of shellfish, shrimp, lobster or crabs and cell wall of fungi. It displays interesting properties as biocompatibility, biodegradability and its degradation products are nontoxic, non-immunogenic. Chitosan is emerging as a potential agent used in enhancing defence mechanism of plant, as growth promoter, as antimicrobial agent, as a soil conditioner. Beside this chitosan is used as carrier for improving nutrient delivery, increasing water use efficiency and as absorbent of heavy metals. This review deals with various sources of chitosan, its methods of production, key aspect of use of chitosan in agriculture, current researches in using chitosan and future implication of chitosan in agriculture.

KEYWORDS: Chitosan, Defence mechanism, Growth Promoter and Soil Conditioner.

INTRODUCTION
Chitosan (pronounced Kite-O-San) discovery can be traced back from 1811 when “chitin”, from which it is derived, was first discovered by Henri Braconnot, who was director of the Botanical Gardens at the Academy of Sciences in Nancy, France. He identified an extract from mushrooms that wouldn’t dissolve in sulphuric acid, which he named ‘fungine’. This was renamed ‘chitin’ a few years later in 1823 when another French scientist called Auguste Odier isolated it from beetle cuticles and named it after the Greek word for ‘tunic’, ‘chiton’. Chitin was the first polysaccharide identified by man, preceding cellulose by about 30 years.

Chitin is poly [β-(1-4)]-N-acetyl-D-glucosamine. It is the most abundant polymer after cellulose. The most important derivative of chitin is chitosan. It is a random linear chain of N-acetyl-D-glucosamine units (acetylated unit) and D-glucosamine (deacetylated unit) joined by β-(1-4) linkages. Conventionally, the distinction between chitin and chitosan is based on the degree of acetylation (DA), with chitin having DA values higher than 50% and chitosan having lower percentages.

Chitin and chitosan are biocompatible, biodegradable, and non-toxic polymers [1]. It has immense unexplored potential which can help in making sustainable agriculture a reality. Chitosan induces callose formation, act as proteinase inhibitors and helps in phytoalexines biosynthesis. Chitosan foliar application increases stomatal conductance and reduces transpiration, without affecting plant height, root length, leaf area or plant biomass. Foliar application of chitosan increases abscisic acid (ABA) content [2]. Chitosan can be used as a seed coating material for cereals, nuts, fruits and vegetables. It alters permeability of the seed plasma membrane, increasing the concentrations of sugars and proline, and enhances peroxidase (POD), catalase (CAT), phenylalanine ammonia-lyase (PAL) and tyrosine ammonia-lyase (TAL) activities [3]. It acts as antifungal [4], antiviral [5] and bionematicidal agent [6]. Chitosan act as carrier promoting slow release behavior of fertilizers [7]. Improves water retention behaviour of soil [8]. Chitosan have the best chelating properties [9], able to remove heavy metal and dye, control algal contamination from lake and acts as a soil conditioner [10]. This review deals with key aspect of use of chitosan in agriculture, current research in this area and future implication chitosan may have in field of agriculture.
SOURCES OF CHITOSAN
Chitin occurs in a wide variety of species, from ciliates, amoebae, chrysophytes, some algae, yeasts and the lower animals like crustaceans, worms, insects and mollusks. Vertebrates, plants and prokaryotes do not have chitosan [11]. Fungi are abundant sources of chitosan and it exists naturally in fungi like zygomycetes and mucorales such as Absidiacoerulae [12], Gongronella butleri, Mucorrouxii [13], Aspergillus niger [14], Rhizopus KNO$_1$ and KNO$_2$ [14]. Aspergillus niger with the highest amount of extractable chitosan obtained at the late exponential phase [14]. But practically chitosan is prepared by chitin deacetylation and its production by Fungus is still an emerging technology.

METHOD OF PREPARATION OF CHITOSAN FROM CHITIN
Chitosan is prepared by 2 methods
1. Deacetylation of chitin

According to Kurita et al., 1993 [15]
Figure 1: Deacetylation method

Process of deacetylation is shown with the help of flow diagram. It is most used method for preparation of chitosan (Figure 1).

2. Fermentation technology
Raw materials most abundantly available for chitin production are the shells of crab, shrimp, and prawn (69- 70%). Chitin is associated with other constituents; chemical treatments are needed for removing impurities. Proteins are removed by sodium hydroxide or by digestion with proteolytic enzymes such as papain, pepsin, trypsin, and pronase. Minerals such as calcium carbonate and calcium phosphate are extracted with hydrochloric acid. Pigments such as melanin and carotenoids are eliminated with 0.02% potassium permanganate at 60°C or hydrogen peroxide or oxalic acid. Conversion of chitin to chitosan generally is achieved by hydrolysis of acetamide groups of chitins by severe alkaline hydrolysis treatment. It is due to the resistance of such groups imposed by the trans-arrangement of the C2-C3 substituent in the sugar ring [16].

Chitosan produced by fungus is of high quality than chitosan produced by crabs, shrimps, due to the degree of acetylation, molecular weight, viscosity and charge distribution of the fungal chitosan. They are more stable than crustacean chitosan. The production of chitosan by fungus in a bioreactor at a technical scale offers additional opportunities to obtain identical material throughout the year. The fungal chitosan is free of heavy metal contents such as nickel; copper [16].
According to Rane and Hoover, [17] and Crestini et al., [18]

**Figure 2: Fermentation method**

Moreover, the production of chitosan from fungal mycelia gives medium-low molecular weight chitosan (1–12 × 10⁴ Da), whereas the molecular weight of chitosan obtained from crustacean sources is high (about 1.5 ×10⁶ Da). For these reasons, there is an increasing interest in the production of fungal chitosan. Preparation of fungal chitosan and crustacean chitosan are explained by flow diagram (Figure 2).

**PROPERTIES OF CHITOSAN**

**Physical and Chemical properties** - Chitosan have rigid D-glucosamine structure, high crystallinity, hydrophilicity weak base. Its deprotonated amino group acts a powerful nucleophile (pKa 6.3) capacity to form hydrogen bonds intermolecularly. It has high viscosity insoluble in water and organic solvents, soluble in dilute aqueous acidic solutions, numerous reactive groups for chemical activation. Cross-linking of chitosan forms salts with organic and inorganic acids. Chitosan possess chelating and complex formation properties, ionic conductivity. Poly electrolytic properties-It is cationic biopolymer with high charge density (one positive charge per glucosamine residue), good flocculating agent, interacts with negatively charged molecules. Molecules entrapment and adsorption properties, filtration, separation, film-forming ability and adhesivity materials for isolation of biomolecules. Biological properties-Important biological properties are biocompatibility, nontoxic, biodegradable, absorbable, bioactivity and antimicrobial activity (fungi, bacteria, viruses).

**Modification of chitosan by graft polymerization**

Chemical modifications of chitosan are studied deeply as it has the potential of increasing its multifaceted applications. With regard to its unique properties such as biocompatibility, biodegradability, and nontoxicity to mammals, it is widely used in fields like biotechnology, pharmaceutics, cosmetics and agriculture. Unfortunately, in spite of having a lot of advantages, its poor solubility in water, low surface area, and porosity of chitosan are the major limiting factors in its utilization. Its solubility is limited at a pH higher than 6.5 where chitosan starts to lose its cationic nature. This problem is probably the major limiting factor chitosan utilization [19].
Grafting of chitosan allows formation of functional derivatives by covalent binding of a molecule, the graft, onto the chitosan backbone [1]. The characteristics of the side chains, including molecular structure, length, and number greatly influence graft copolymer properties. The free amino groups on deacetylated units and secondly, the hydroxyl groups on the C3 and C6 carbons on acetylated or deacetylated units are 2 groups that can be grafted. Chitosan would obtain much improved water solubility and bioactivities such as antibacterial and antioxidant properties after grafting. Grafting chitosan is a common way to improve chitosan properties such as increasing chelating or complexation properties, bacteriostatic effect or enhancing adsorption properties. Figure 3 showed structure of chitosan particle.

CHITOSAN IN AGRICULTURAL CONTEXT

Plant Defense Mechanism
Plants respond naturally against biological and environmental stress condition, but sometimes induced defence is needed against harder threats. Chitosan is a great polymer induces defence actions, and responses against pathogens attack. Phytoalexines and pathogenesis related proteins (PR), protein inhibitors, chitinases, glucanases, Reactive Oxygen Species (ROS) and hydrogen peroxid generation are favoured in presence of chitosan [20]. Chitosan interacts with cellular DNA generating multiple biochemical reactions in the plant, a rapid response in the plant against pathogens attack, thus considered as an elicitor, (a defence mechanism activator in plants). Responses of plants to the onset of stress by pathogen infection are considered as an indication of resistance. Chitosan concentration at 2-4 g/liter resulted in a positive effect on endogenous hormone content, alpha-amylase activity and chlorophyll content in seedling leaves of maize [21]. Chitosan increases, chitinase and chitosanase activity in turmeric plants provide enhanced resistance against Pythium aphanidermatum infection, [22]. Chitosan induces callose formation in soybean and parsley cells, proteinase inhibitors in tomato leaves and phytoalexines biosynthesis in pea. The elicitor activity of chitosan seems to be mediated through the interaction of this polycationic molecule with negatively charged phospholipids, rather than a specific interaction with a receptor-like molecule.

As Plant Growth Promoter and combating abiotic stress
Chitosan acts as plant growth promoter in some crops like Faba bean plant, radish, passion fruit, potato, gerbera, cabbage, soybean and other crops when it is incorporated in solution. It increases plant production and protects plants against pathogens. Chitosan has a significant effect on growth rates of roots, shoots, flowering, and number of flowers. These molecules are strongly hydrophilic and alleviate stress damage in plant cells by reducing the water potential and increasing the activities of some biological macro molecules. Growth of orchids (Dendrobium and Cymbidium respectively) was enhanced when chitosan was supplied to micro propagated plants growing under aseptic condition [4]. Significant improvements in growth have been reported in daikon radishes (Raphanussativus), soybean sprouts, cabbage (Brassicaoleracea), sweet basil [7]. Chitosan enhances rice seedling growth via gene expression network between nucleus and chloroplast. Combination of chitosan and plant growth promoting rhizobacteria can be used as biofertilizers to improve the maize production [9]. It is used as a biostimulator in the cultivation of potted freesia [23]. And enhances phytochemical levels, enzymatic and antioxidant activity of spinach leaves by chitosan treatment. Chitosan based superabsorbent delayed wilting of alfalfa plant by 6-10 days improves stress tolerant trait of plant [24]. An overview of use of chitosan in agriculture was given in table 1 and 2.
### Table 1 - Important use of chitosan in agriculture

<table>
<thead>
<tr>
<th>Chitosan use</th>
<th>References</th>
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<tbody>
<tr>
<td>Promoting plant defense mechanism</td>
<td>[4], [22]</td>
</tr>
<tr>
<td>As plant growth promoter and combating abiotic stress</td>
<td>[23], [26]</td>
</tr>
<tr>
<td>As antitranspirant</td>
<td>[2]</td>
</tr>
<tr>
<td>Seed coating /priming</td>
<td>[3], [4]</td>
</tr>
<tr>
<td>As antifungal agent</td>
<td>[26], [27], [28], [4]</td>
</tr>
<tr>
<td>As antiviral agent</td>
<td>[5], [15]</td>
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<tr>
<td>Bionematicide</td>
<td>[29]</td>
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<tr>
<td>Post-harvest management</td>
<td>[30], [31]</td>
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<tr>
<td>Nutrient delivery carrier</td>
<td>[30], [32]</td>
</tr>
<tr>
<td>Water retention in soil</td>
<td>[33], [7]</td>
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<tr>
<td>Heavy metal remediation in soil</td>
<td>[8], [9]</td>
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<tr>
<td>As soil conditioner</td>
<td>[10], [31]</td>
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<tr>
<td>Waste water treatment</td>
<td>[35]</td>
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<tr>
<td>Dye</td>
<td>[36], [37], [38]</td>
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<tr>
<td>Heavy metal</td>
<td>[39]</td>
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<tr>
<td>Algal bloom</td>
<td>[40]</td>
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</tbody>
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### Table 2 - Chitosan use in abiotic stress

<table>
<thead>
<tr>
<th>Crops</th>
<th>Stress</th>
<th>Mechanism</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wheat</td>
<td>Osmotic stress</td>
<td>Seed germination root and shoot growth, increases vigour</td>
<td>[41]</td>
</tr>
<tr>
<td>Maize</td>
<td>Low temperature stress</td>
<td>Decline in malondialdehyde (MDA) contents, relative permeability of the plasma membrane and an increase in the soluble sugars, proline, peroxidase (POD) and catalase (CAT) activities were detected both in the chilling-sensitive and chilling-tolerant maize seedlings after priming with chitosan</td>
<td>[3]</td>
</tr>
<tr>
<td>Chickpea</td>
<td>Salinity stress</td>
<td>Reduces the harmful effects of salinity via either reduction in Na+ absorption or by accumulation of proline, total carbohydrate and K+</td>
<td></td>
</tr>
<tr>
<td>Ajowan</td>
<td>Salinity stress</td>
<td>Seed germination seedling growth</td>
<td>[42]</td>
</tr>
<tr>
<td>Lentil</td>
<td>Salinity stress</td>
<td>Seed germination seedling growth increases</td>
<td>[43]</td>
</tr>
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</table>

**As antitranspirant**

Chitosan foliar application increases stomatal conductance and reduces transpiration, without affecting plant height, root length, leaf area or plant biomass. When chitosan was sprayed in leaves, abscisic acid (ABA) content increases which control opening of stomata [2]. Water use of pepper plants treated with chitosan reduced by 26%–43%, chitosan has potential to be developed as an anti transpirant in agricultural situations where excessive water loss is undesirable. Both ABA and jasmonic acid have both been found to raise in concentration in response to chitosan treatment and these hormones are involved in control of opening of stomatal aperture.

**Seed coating/ priming**

Chitosan can be used as a seed coating material for cereals, nuts, fruits and vegetables. It alters permeability of the seed plasma membrane, increasing the concentrations of sugars and proline, and enhances peroxidise (POD), catalase (CAT), phenylalanine ammonia-lyase (PAL) and tyrosine ammonia-lyase (TAL) activities [3]. Germination rates of seeds increases significantly and seedlings germinate quicker, better, and are vigorous. Seed soaked with chitosan had increased the energy of germination, germination percentage, lipase activity, and gibberelic acid (GA₃) and indole acetic acid (IAA) levels in peanut. Seed priming in maize increases chilling tolerance. Priming with chitosan reduced the relative permeability of the plasma membranes of the maize under low temperature leads to less damage from low temperature stress [3]. The decline of malon dialdehyde (MDA) which is an indicator of lipid per oxidation is also induced by chitosan coating due to increase in antioxidant activity.

**As Antifungal agent**

Chitosan inhibited the radial and submerged growth of *Alternaria solani* at 1 mg/ml, and controls tomato plants from blight pathogen. Soil amendment with chitosan has repeatedly been shown to control fungal
diseases in numerous crops, especially Fusarium wilts and grey mould [45]. The control of oomycete pathogens has also been achieved with chitosan treatment, with Phytophthora capsici on peppers [46] and Phytophthora infestans in potato, the control of Phytophthora capsici in peppers was due to the disruption of the endomembrane system, especially the integrity of the vacuoles caused by chitosan. It controls Alternaria blight in tomato [28], damping off [27], and inhibited growth of Fusarium oxysporum f. sp. Tracheiphilum causing morphological changes [26].

As antiviral agent
Chitosan has been shown to control viral diseases in plants [5]. However, it is not yet confirmed that viruses are directly inactivated by chitosan, which in itself would appear to be unlikely as viruses are not composed of chitin or related polysaccharides. Therefore, rather than direct toxicity, it has been proposed that chitosan is effective against plant viruses by modifying the plant’s response to infection. Hypersensitivity response is developed in plant check viral particle transfer by chitosan application, also reported similar observations with the potato virus X, tobacco mosaic and necrosis viruses, alfalfa mosaic virus, peanut stunt virus, and cucumber mosaic virus.

Bionematicide
Chitosan, applied in soil promote chitinolytic microorganisms which destroy nematode eggs and degrades the chitin containing cuticle of young nematodes. Because of the high content of nitrogen in chitosan, concentrations of ammonia emissions increase turning toxic to nematodes. Chitosan displayed elicitor activity by inducing local and systemic resistance mechanisms of tomato plants against the root-knot nematode Meloidogyne incognita. Low molecular weight chitosan controls M incognita in better way [47].

Pinewood nematode (Bursaphelen chusxyphilus) a stem nematode is controlled by chitosan as it causes alteration in bacterial community which support nematode colony to prosper, i.e. gram negative to gram positive bacteria altering its reproduction capacity and increase its mortality [6]. Chitosan enhance parasitism of Meloidogyne javanica eggs by the nematophagous fungus Pochonia chlamydosporia increases appressorium differentiation in Pochonia chlamydosporia [29].

Post harvest treatment
Chitosan coating has ability to modify internal atmosphere in the tissue and fungistatic property has a potential to prolong storage life and control decay of fruits. In fruits and vegetables, chitosan provides more firmness and it promotes diminution of the normal microbiological charge [48]. Increasing the product life. Chitosan coating is likely to modify the internal atmosphere without causing anaerobic respiration, since chitosan films are more selectively permeable to O₂ than to CO₂. Effective in maintaining the pulp color, indicating the reduced ripening process and extended storage life of mango cv. Alphonso fruits. Controls Post harvest Decay on Cherry Tomato Fruit Possibly via the Mitogen-Activated Protein Kinase Signaling Pathway [49].

Nutrient delivery carrier
Chitosan act as a carrier enhancing slow release behaviour of fertilizer, prevent leaching, fixation losses due to rapid mobility, high solubility. A lot of research is going on in this field. Chitosan has the potential to improve fertilizer’s degradation rates in order to obtain slow-release properties [50]. A chitosan coated NPK fertilizer and found that nutrient release mechanism from fertilizer is non – Fickian and is controlled by a combination of diffusion of fertilizer from coating material and degradation rate of chitosan. A controlled release phosphorus fertilizer was prepared using chitosan and citric acid a cross linker and it was found that its slow release behaviour increases with chitosan coating [32]. Chitosan nano particle suspension having NPK fertilizer was studied and FTIR results indicated the existence of electrostatic interactions between –COO⁻ and –NH₃⁺ of the chitosan nano particles and the elements N, P and K present in the urea, calcium phosphate, potassium chloride, respectively. The stability of the chitosan metha acrylic acid colloidal suspension was higher with the addition of nitrogen and potassium than with the addition of phosphorus, due to the higher anion charge from the calcium phosphate than the anion charges from the potassium chloride and urea [51]. Encapsulation of urea was performed in chitosan microspheres via emulsification followed by cross-linking with genipin, a natural cross-linker and it was found that increasing urea content increases the release rate while increasing cross linker and chitosan promote slow release behaviour [30]. Potassium-containing chitosan-montmorillonite microspheres were prepared using a coagulation method and very high levels of fertilizer were sorbed on to the material. Chitosan montmorillonite microsphere-containing potassium showed two specific periods of fertilizer release. Enhancement of nitrogen release properties of urea–kaolinite fertilizer with chitosan binder was studied by [52].

Super water-absorbing material from chitosan, EDTA and urea was found useful in agriculture for controlled release of water urea and micronutrients increasing fertilizer use efficiency [33]. Chitosan has gel forming properties and it can be used for preparation of hydrogel. Chitosan is an excellent biodegradable biomass and can be degraded into nontoxic products in vivo. It has both reactive –NH₂ and –OH that can be convenient for graft polymerization of hydrophilic vinyl
monomers onto it under mild reaction condition, and the acquired superabsorbent resin can absorb aqueous solution hundreds of times than their own dry sample. Sodium humate along with chitosan could enhance water absorbency and the content of 10 wt% sodium humate gave the best absorption [3]. A novel chitosan-g-poly (acrylic acid)/montmorillonite superabsorbent nanocomposite showed water absorbency of 160.1 g g⁻¹ in distilled water and 46.6 g g⁻¹ in 0.9 wt % NaCl solution prepared by in situ intercalative polymerization among chitosan, acrylic acid, and montmorillonite. Chitosan coated fertilizer showed water absorbency of the 70 times its own weight if it was allowed to swell in tap water at room temperature for 90 min [8].

**Heavy metal remediation in soil**

Chitosan and treated chitosan were able to bind metal ions, even in the presence of K⁺, Cl⁻ and NO₃⁻, which are dominant ions in soil. Therefore, remediation of metal contaminated soil using chitosan and cross-linked treated chitosan as soil amendments is feasible. Nitrogen is main binding site and formation of co-ordination bonds, which may change the arrangement of the polymer and increase the disorder of the polymer network may be a reason for complexation of metal with chitosan [9]. Chitosan is proved to have the best chelating properties among other natural polymers. Functional group responsible for complex formation is amino groups among chitosan, in which nitrogen is a donor of electron pairs, although hydroxyl groups may also participate in sorption. The mechanism of combining these reactive groups with ions of metals is much differentiated and can depend on the ion type, pH, and also on the main components of the solution. The complexes formation could be also described based on Lewis acid-base theory: metal ion (acting as the acid) is the acceptor of a pair of electrons given by chitosan (acting as the base). The selectivity of mixtures of the ions Cu²⁺>Hg²⁺>Zn²⁺>Cd²⁺>Ni²⁺>Co²⁺ and Ca²⁺. Application of chitosan with 1.15 g kg⁻¹ soils of 7 days could improve the remediation of the soil contaminated by Hg (II) and Cr (VI) in the industrial application.

**As soil conditioner**

Being a polysaccharide, chitosan acts as a bioremediator molecule that stimulates the activity of beneficial microorganisms in the soil such as *Bacillus spp.*, *fluorescent Pseudomonas spp.*, Actinomycetes, Mycorrhiza and Rhizobacteria. This alters the microbial equilibrium in the rhizosphere promoting beneficial microorganisms. The chitosan treatment alongside mycorrhizal inoculation aided the bioremediation of soil polluted with a range of heavy metals by Elsholtzia splendens [10]. Encapsulating a consortium of different PGPR within chitosan helped in delivery and stimulated the growth and activity of the bacteria for bio augmentation and bio stimulation of hydrocarbon-polluted soils. A study on crude oil contaminated seawater found that chitin/chitosan encapsulation improved the effectiveness and survival of bio remediating chitinolytic bacteria [53]. It may be possible to utilize the cationic nature of chitosan to boost a soil/growing medium’s anionic exchange capacity (AEC), which are generally low and far lower than their cationic exchange capacity (CEC). Soils treated with chitosan could suffer less from leaching of anionic nutrient fertilizers, such as nitrates and phosphates, but this hypothesis remains untested. The bacterium *Bacillus subtilis* is a pathogen of fungi and is one of the most widely used bio pesticide in agriculture. *B. subtilis* known to secrete chitinases into the medium in which it is growing [34]. The addition of chitosan to the carrier material improved the multiplication of *B. subtilis* and improved the bacteria’s fungicidal action and improved the control of *Fusarium* wilt in pigeon pea and crown rot in peanut caused by *Aspergillus niger*. Chitosan addition also improved the action of *B. subtilis* against powdery mildew in strawberry [35]. It also enhances water retention behavior of soil indirectly conditioned the soil [24].

**Waste water treatment**

Chitosan can be used as an adsorbent to remove heavy metals and dyes due to the presence of amino and hydroxyl groups, which can serve as the active binding sites in waste water. Amino groups of chitosan can be cationized, after which they adsorb anionic dyes strongly by electrostatic attraction in the acidic media. To improve chitosan’s performance as an adsorbent, cross-linking reagents such as glyoxal, formaldehyde, glutaraldehyde, epichlorohydrin, ethylene glycondiglycidyl ether and isocyanates have been used [36]. Cross-linking agents do not only stabilize chitosan in acid solutions so that it becomes insoluble but also enhance its mechanical properties.

**Dye**

Synthetic dyes consist of two main groups of compounds—chromophores and auxochromes. Chromophores determine the colour of the dye while the auxochromes determine the intensity of the colour. Dyes have become one of the main sources of severe water pollution as a result of the rapid development of the textile industries. The chitosan composites had a comparable adsorption for methylene blue and reactive dye (RR22), in comparison to chitosan beads. Prepared cross-linked chitosan/bentonite composites to adsorb tartrazine, a dye which contains azo group that is harmful to living beings. The chitosan composites, cross linked with epichlorohydrin were able to improve the
chitosan performance as an adsorbent [36]. Found cross linked chitosan/oil palm composite beads have good efficiency to remove Reactive Blue 19.

**Heavy metals**

Chitosan/ceramic alumina composites act as an adsorbent to remove anionic and cationic heavy metals such as As(III) As(V) Cu(II) and Ni(II). Cr(VI). Chitosan composites help in removal Cr from leather industry [55]. Chitosan hydrogel film, cross-linked with glyoxal (Fe₃O₄NPs/CS/glyoxal), used as adsorbent for 80–90 % removal of toxic Cr(VI) from water [39].

**Algal Bloom.**

Chitosan is known to be a non-toxic flocculant. The most likely mechanisms involved in this coagulation are adsorption and charge neutralization. Chitosan has a net positive charge because of the high charge density of the chitosan. As the overall charge of microalgae cells is negative, the positively charged chitosan is strongly adsorbed on microalgae cells, which results in most of the charged groups being close to the surface of the cells and effectively destabilize the microalgae. Chitosan first neutralizes charges on the microalgae cells, weakens the electrostatic repulsion between the microalgae cells, and then reduces the inter particle repulsion; such effect is called charge neutralization. Shao et al. 2011 [40] studied the physiological responses of Microcystis aeruginosa under the stress of chitosan modified kaolinite (CMK). When flocculated with CMK, Chl a, carotenoids, phycocyanin, and allophycocyan in were much lower. This indicated that high level of CMK could cause cellular membranes damage and then the intracellular substances leakage and finally could cause the death of M. aeruginosa.

**CONCLUSION**

Chitosan use in agricultural field is fetching great attention as antimicrobial agent, plant growth promoter, as edible film for coating of fruit and vegetable. It can be used as fertilizer sources enhancing water retention capacity of soil. The area of chitosan research in agriculture is still at its nascent stage requires much more attention for its promotion. Encouraging and promising results are already being achieved in delivery of agrochemicals, in waste water treatment and as growth promoter. The use of such materials for the delivery of pesticides, micronutrients and fertilizers is expected to reduce the required dosage for efficacy and ensure a controlled delivery. However, issues such as increasing the scale of production processes and lowering costs, as well as toxicological perspectives, still must be addressed to further advance chitosan into sustainable agriculture. While research interest into chitosan based delivery systems is increasing, the current level of knowledge does not allow a fair assessment of the pros and cons that will arise from the use of chitosan based products in agriculture. Overall, it can be concluded that chitosan-based technology has a promising future with value in crop productivity in sustained and eco-friendly ways.

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