STM JOURNALS

International Journal of
Antibiotics

https://journals.stmjournals.com/ijab

Volume 1, Issue 1, 2024
January—June
DOI (Journal): 10.37591/IJAB

Review IJAB

Environmental Implications of Chitosan Nanostructures

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Abstract

Chitosan (CS), as a biopolymer, has unrivalled chemical and mechanical modification capabilities to develop novel characteristics, functions, and applications, particularly in the manufacture of cutting-edge membrane adsorbents. Membrane adsorbents utilizing carbon starch (CS) have emerged as a viable and efficient engineering instrument for eliminating diverse pollutants from aquatic settings, including heavy metals and dyes. To date, much study has been directed towards improving the adsorptive characteristics, permeability, physicochemical stability, and sustainability of CS-based membranes through the use of various types of nanoparticles (NPs). Additionally, nanoparticles (NPs) can be applied to personalise the appearance and performance of nano-structured and nano-fibrous membranes made from chitosan (CS). This chapter focuses on the utilisation of various types of nanoparticles in CS-based membrane adsorbents, comprising four major groups of metal-based, non-carbon mineral, carbonic (carbon-based), and Metal Organic Frameworks (MOFs). The review and discussion have been broadened to cover manufacturing methods and the effects of adding nanoparticles (NPs) on the chemistry, morphology, adsorption kinetics, and removal effectiveness of membranes made of chitosan (CS). This review might help researchers choose appropriate NP modifiers and preparation procedures for synthesising Nano composite CS membrane adsorbents for varied applications. Advances in chitosan modification, primarily with nanomaterials such as multi-walled carbon nanotubes and nanoparticles (TiO_2, Ag, S, and ZnO), and their application for environmental remediation.

Keywords: Chitosan, nanoparticles, nano-structured membranes, nano-fibrous membranes and Metal Organic Frameworks (MOFs)

INTRODUCTION

Biologically derived macromolecules, such as those found in plants and animals, are known as biopolymers. Different isolated compounds provide a variety of purposes, including the storage and transport of information and the provision of integrity in the form of hard shells. Biopolymers are polymers derived from living organisms like plants and bacteria, as opposed to the traditional source of polymers, which is petroleum. Biopolymers' principal sources are renewable [1]. Many, but not all, biopolymers are biodegradable, which implies they are capable of degrading into water, carbon dioxide, inorganic chemicals, methane, or biomass by the enzymatic action of microorganisms [2]. Chitin, one of the most prevalent biopolymers in nature, serves as the origin for the natural polysaccharide biopolymer known as chitosan (CS). Chitosan, a sugar derived from the exoskeletons of shellfish such as shrimp, crab, and lobster, is employed in pharmaceuticals and medicinal applications. Additionally, chitosan a fibrous material, has the potential to decrease the absorption

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Received Date: January 19, 2024
Accepted Date: January 23, 2024
Published Date: January 31, 2024

Citation: Rakshita Chaudhary, Prerna Banerjee, Nisha Gaur, Surabhi Bajpai, Kapil Joshi. Environmental Implications of Chitosan Nanostructures. International Journal of Antibiotics. 2024; 1(1): 42–58p.

of dietary fats and cholesterol within the body [3]. When administered to wounds, it also aids in blood clotting. The most abundant functional groups in the structure of CS are amine and hydroxyl. The electron lone pairs of oxygen and nitrogen atoms are typically responsible for the adsorption reactivity of CS-based adsorbents. The hydroxyl groups in the chitin structure, which are the source of CS, can be used to convert chitin to CS [4]. The adsorption of heavy metals in the blend relied on both complexation and the strong attraction between the hydroxyl groups within the cellulose/chitin blend and metal cations. Aside from cation adsorption, CS composite adsorbents have been employed to remove anions from aquatic environments. Biopolymer/mixed metal oxide composites are potential fluoride removal adsorbents [5]. In another study, they created a rod-shaped Ca-Zn at chitin composite for fluoride adsorption. The bimetallic oxide/chitin composite was found to be porous and F anion adsorptive. The most likely mechanism for adsorption was identified as electrostatic ion-dipole interaction between calcium and fluoride [6, 7].

A study reported that a new insight into CS-based membranes for the elimination of heavy metals from water have emerged [8]. These findings affirm that the utilisation of appropriate copolymers and the incorporation of suitable biomaterials can enhance the separation efficiency and industrial applicability of CS membranes [9]. Membranes based on CS (chitosan) have emerged as highly promising methods for the adsorption of emerging contaminants. These contaminants include compounds originating from synthetic or natural sources that have recently come to light or are actively monitored in the environment [10]. In terms of stability, crucial attributes for CS-based adsorptive membranes encompass chemical, thermal, and mechanical resistance. Enhancing the chemical and mechanical resilience of CS- based adsorptive membranes can be achieved by incorporating CS with compatible copolymers like polyvinyl alcohol and cellulose derivatives [11]. In their review, E. Salehi et al. (2022) examined the manufacturing and characterisation techniques applied to CS- based membranes, with particular attention to membranes blending CS with polymers [12]. In general, the trade-off between permeability and selectivity is a fundamental issue in the commercialization of membrane separation. Another important issue that impedes the usage of CS-based membranes in an acidic environment is the low stability of CS in acidic solutions. The protonated amino groups of CS in the acidic environment produce high electrostatic repulsion among CS molecules. It is preferable to improve polymer characteristics and incorporate new functions in order to meet the realistic use of CS-based membranes [13]. Metal-based NPs, MOFs, carbon-based NPs, and non-carbon mineral NPs are among the active species employed in membrane modification. Metal-based NPs with oxidative activity, such as Fe_2O_3, can improve the adsorptive properties of CS-based membranes. As a result of the degradation of organic materials on the catalytic membrane surface, carbon-based NPs can inactivate bacteria and increase membrane permeability. MOFs and non-carbon minerals' crystalline and extremely porous character can aid to increase the surface area and adsorption capacity of CS-based membranes [14]. The primary consideration for selecting nanoparticles (NPs) is to improve both the separation efficiency and the physicochemical stability of the resulting composite membranes. Incorporating NPs into membranes enhances permeability, tensile strength, pH tolerance range, mass transfer rate, and selectivity while simultaneously mitigating membrane fouling [15]. Metal-based nanoparticles are preferred for incorporation into chitosan-based membranes due to the formation of a nanostructure interconnected network of CS-NPs, which can enhance permeability and selectivity. In fuel cell applications, metal-based nanoparticles find utility in proton-exchange membranes. Non-carbon minerals are the preferred choice among nanoparticles for environmental remediation and saltwater desalination due to their minimal toxicity and high capability to absorb solutes at the molecular scale [16]. Adsorptive membranes incorporating Metal-Organic Frameworks (MOFs) demonstrated excellent performance in effectively eliminating micro-pollutants like dyes and heavy metal ions. Another reliable method for creating Nano composite adsorbents capable of absorbing trace levels of organic and inorganic contaminants from aquatic environments is the use of carbon-based NPs to alter CS membrane adsorbents. Carbon-based NPs have been identified as possible candidates for the preparation of Nano composite CS-based membranes due to their mechanical stability, large specific surface area, and a long history of study in the background. While nanoparticles (NPs) have the potential to enhance the characteristics of CS membrane absorbents, incorporating them into the polymer matrix raises various concerns [17]. These concerns encompass them into the polymer matrix raises various concerns. These concerns encompass the risk of NP leakage leading to secondary contamination of the filtrate, achieving uniform dispersion within the polymer matrix while ensuring compatibility with the polymer background, determining the ideal NP concentration, managing economic feasibility, and addressing selectivity issues, especially when targeting selective adsorption [18]. Two fundamental and commonly employed methods for producing membrane adsorbents based on chitosan (CS) involve the processes of solution casting/solvent evaporation and phase inversion, often followed by chemical activation of the resulting membrane. Moreover, the self-assembly process for creating CS-based composites has demonstrated its effectiveness and reliability. Numerous studies have indicated that self-assembly represents a straightforward method for developing innovative composite materials with outstanding adsorption capabilities. This study provides an in-depth exploration of recent advancements in CS-based membrane adsorbents that incorporate nanoparticles (NPs) [19]. The paper will encompass discussions on the chemistry, morphology, preparation techniques, isothermal research findings, and adsorption kinetics of CS-based membrane adsorbents modified with various types of nanomaterials, including metal-based, MOFs, carbon-based, and non-carbon-based NPs.

According on the survey results, non-carbon mineral NPs are more commonly used in CS membrane adsorbents than carbon-based NPs, metal-based NPs, and MOFs. Non-carbon minerals have received more attention than other NPs due to their cost-effectiveness, environmental friendliness, scientific maturity of synthesising methodologies, and ability to achieve superior separation performance. Recent and future initiatives, on the other hand, reveal a somewhat different pattern, with rising interest in adjustable nanostructures such as metal organic frameworks for the alteration of membrane adsorbents. To enable the industrialization of membrane adsorption processes, researchers must simultaneously focus on important factors such as process sustainability, techno-economic favourability, and separation performance desirability [20].

CAPPED NANOPARTICLES

Nanoparticles are defined as particles with a size between 1 and 100 nm and with characteristics distinct from those of the bulk material. Nanoparticles have been used in numerous applied scientific fields during the past few decades. Nanoparticles can be created using both "top-down" and "bottom-up" processes. The first uses energy to achieve nanonization, whereas the other uses physicochemical control to build the nano-capsule by accumulating monomers, molecules, ions, or even atoms. On a commercial basis, uncapped nanoparticles of greater size are typically generated in huge quantities. When released as big aggregates, these nanoparticles pose a threat to the environment [21]. The stabilisation of colloidal solutions and their absorption into living cells and the environment therefore depends on the selection of appropriate capping moieties. The surface chemistry and size distribution of nanoparticles undergo alterations when they are coated with biocompatible surfactants. Capping agents must be biodegradable, extensively dispersed, bio-soluble, biocompatible, and non-toxic in order to work successfully in living systems [22]. As a result, their general contact with biological elements is reduced, which minimises cellular toxicity. The assessment of nanoparticles' possible medicinal effects and environmental impact is of tremendous interest to scientists. Surface capping improves nanoparticles' biological characteristics. Emerging therapeutics known as capping agents exhibit clinical value in concert with the biocompatible nanoparticles to which they have been bonded. The steric barrier caused by the covalent interaction between the chains of capping ligands and the surface of the nanoparticles gives the nanocomposite its ultimate stability [23]. Colloidal suspensions of nanoparticles are considerably altered by capping agents, which makes them desirable candidates for biological applications including medication administration and theranostics in cancer. The surface chemistry, shape, and size of nanocrystals—which are related to the right capping moieties—define their biological reactivity and functioning with limited side effects. Due to the new properties that the tiny nanoparticles' surface tailoring produced, they have been investigated in biomedicine and environmental cleanup [24]. The creation of capped nanocomposites with improved colloidal stability and biological functions is discussed in this study. Figure 1 shows the covalently bounded nanoparticles with capping agent.

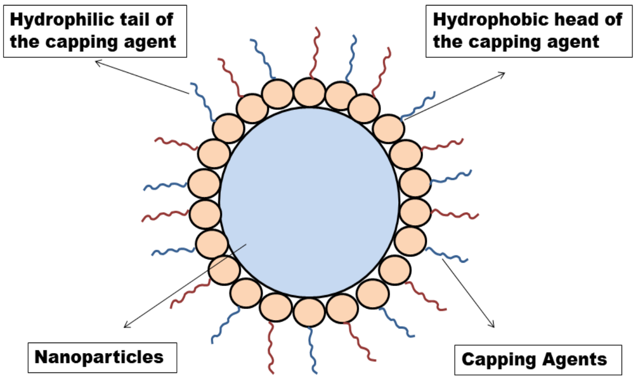

Figure 1. Covalently bounded nanoparticles with capping agent.

Capped Nanoparticles Impact on Biomedicine

Capping or stabilising compounds are required in the manufacturing of nanoparticles to improve their biomedical functioning by lowering toxicity and increasing biocompatibility and bioavailability in living cells. They inhibit nanoparticle clusters or aggregates, improve colloidal stability, and prevent uncontrolled growth of nanoparticles (particularly metal and metal oxide nanoparticles). The various types of capping agents also influence particle size and morphology, as well as magnetic, optical, and catalytic properties. The bio conjugate of nanoparticles is critical. Figure 2 shows the different areas of Nanoparticle Biomedical Application. As potential capping agents, biocompatible, non-toxic, and biodegradable moieties are used [25]. As illustrated in Figure 2 the capped nanoparticles have been widely explored for their applications in biomedicine, including antibacterial, antioxidant, anticancer, and antidiabetic effects. For biomedical applications such as cancer therapy medication delivery and antibacterial activity [3].

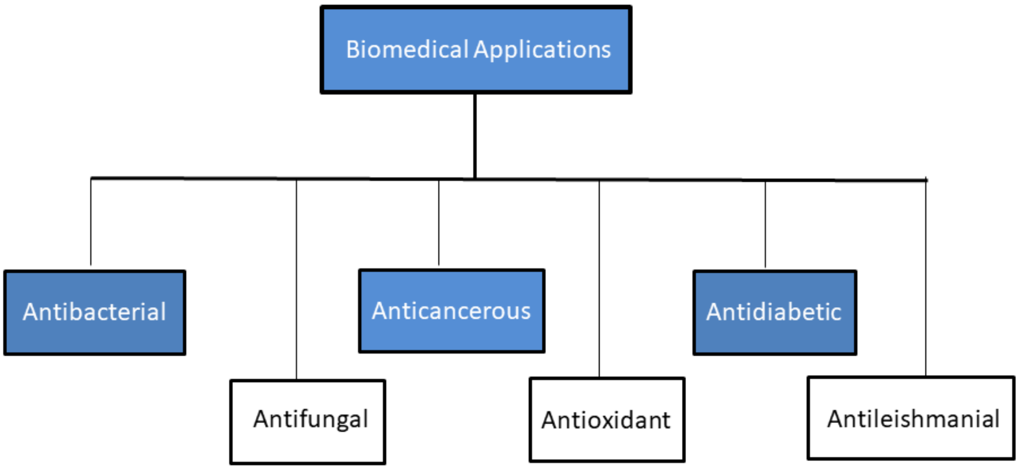

Figure 2. Different areas of nanoparticle biomedical application.

ANTIMICROBIAL ASPECTS OF CHITOSAN BASED CAPPED NANOPARTICLES

Around the world, infectious diseases are primarily caused by microbes. The development of microbial illnesses is being fought against by researchers from all over the world. For example, commonly used conventional medications cannot demonstrate their efficacy against microbial infections. The most frequent cause of this is the abuse of these medications, which makes bacteria resistant to them [26]. Additionally, some antimicrobial medications are extremely irritating and poisonous, therefore researchers are paying close attention to finding new approaches to create antimicrobial compounds that are both safe and affordable. Currently, the most active study field in healthcare is the prevention and suppression of microbial infections. This encourages the creation of new, highly effective materials with outstanding antibacterial characteristics [11]. Nanotechnology serves as a suitable replacement for this. Monodispersed nanoparticles have been extensively studied in the pharmaceutical sector for the treatment of antimicrobial diseases. Numerous kinds of nanoparticles are used as antibacterial agents today. For instance, the greater solubility and release of Ag^{+1} ions in chitosan functionalized silver (Ag) nanoparticles resulted in improved antibacterial activity [27]. A clever antifouling agent, spherical Ag nanoparticles functionalized with core-shell magnetic chitosan microspore showed effective antibacterial action. The fungicidal activity of Ag nanoparticles coated with PVA/aminopropyltriethoxysilane was better. Ag nanoparticles, ZnO nanoparticles, and CuO nanoparticles modified with PVP and PEG all shown strong antibacterial properties. Additionally, the antibacterial activity of Ag nanoparticles functionalized with EDTA, PEG, PVP, and PVA was examined. The findings demonstrated that PVP coated Ag nanoparticles, which are smaller than other coated nanoparticles, have greater antibacterial action [8, 11]. Table 1 summarises a few capped nanoparticles and their uses in the biomedical field.

Table 1. The capping agents with different biological functions.

Capping agents	Nanoparticles	Biological activity
Chitosan	Liposomes	Antidiabetic
Parkia speciosa extract	Ag	Antioxidant
PVA	Ag	Anticancer
PEG	TiO_2	Anticancer
Chitosan	ZnO	Antibacterial, Abtioxidant, Antidiabetic, Cytotoxic
Chitosan	FeO	Antibacterial and Antioxidant
Chitosan+PEG+PVP	Fe_3O_4	Anticancer drug delivery
PVP	WO_3	Anticancer
PVA	Mg	Anticancer
PVA/Guar Gum	Fe_3O_4	Anticancer
PVA	Cu	Antibacterial
Aloe vera extract	Fe_3O_4	Anticancer
Cellulose	Ag	Antibacterial
Alginate	ZnO	Antibacterial
Ethylene glycol	ZnO	Antifungal
Dodecanethiol	Ag	Antifungal

CHITOSAN AND ITS MODIFICATION

Chitin, an unbranched, glucose-based polysaccharide that is abundant in the major components of fungi, crustacean, and insect exoskeleton cell walls as well as some bacterial and fungal cell walls, is the source of the partially deacetylated polymer known as chitosan [28]. Figure 3 illustrates the linear, - (1, 4)-linked N-acetylglucosamine units that make up chitosan. The origin, separation, and level of deacetylation of the chitin determine the chitosan's quality**.** Chitosan also demonstrates crystallinity and polymorphism, depending on the origin of the polymer and treatment during the extraction process. The maximum crystallinity was found in chitin, which was 0% deacetylated, and in fully deacetylated chitosan, which was 100% deacetylated.[3] Chitosan with a straight, unbranched shape and a higher molecular composition increases viscosity in acidic situations. Figure 3 shows the chitin's partial acetylation results in the formation of chitosan. In contrast to other polysaccharides (cellulose or starch), chitosan's chemical structure allows for unique changes because of a powerful electrostatic attraction mechanism that can be used to create polymers for specialised uses [29].

The Fundamental of Adsorption Process

Adsorption is the process by which a molecule moves from the main body of a fluid (gas or liquid) towards a solid surface. Surface interactions between the adsorbate and the active sites, mediated by physical forces or chemical bonds, enhance adsorption. The thermodynamic requirement for adsorption is that the attractive energy of the solid surface be larger than the cohesive energy of the molecules that will be adsorbate [30].

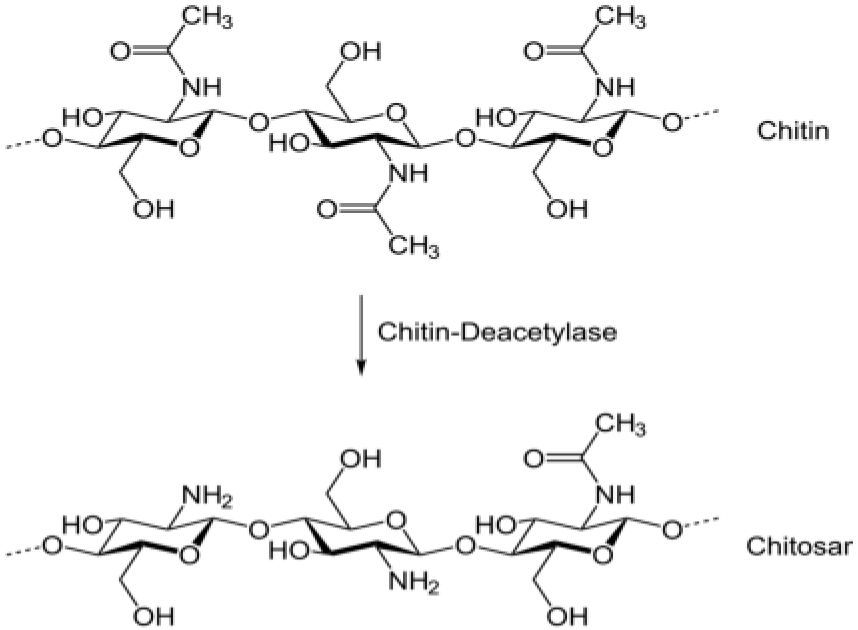

Figure 3. Chitin's partial acetylation results in the formation of chitosan [29]

Chitosan Modified Metal Organic Framework (MOFs)

A category of nanostructures known as metal-organic frameworks (MOFs) is composed of metal ions or clusters that are joined by organic ligands. Due to MOFs' large specific surface area and ease of access to their inner structure, the synthesis of improved adsorbents has advanced dramatically. It has been demonstrated that MOFs increase the stability, hydrophilicity, and dispersibility of CS-based membranes [31].

Chitosan modified with CNTs (Carbon Nanotube)

Lijima in 1991 was the first to discover carbon nanotubes (CNTs). Because of their nanoscale size and distinctive features, carbon nanotubes, which are carbon allotropes and include diamond, graphite, and graphene, have become important in the subject of nanotechnology. They are quite interesting because they are straightforward and simple to synthesise [32]. Single-walled carbon nanotubes (SWCNTs), double-walled carbon nanotubes (DWCNTs), and multi-walled carbon nanotubes (MWCNTs) are the three primary forms of CNTs. SWCNT is a layer of graphene sheet that has been rolled into a single cylinder; DWCNT is a layer of graphene sheet that has been rolled into two cylinders; and MWCNT is a layer of graphene sheets that has been rolled several times [33]. Van der Waals interactions, which cause CNTs to bundle and result in the creation of huge aggregates, hold these folded graphene sheets together. When created, CNTs are less dispersive and insoluble materials. Figure 4 shows the different methods for functionalization of carbon nanotubes. For improved solubility in the majority of solvents, higher chemical reactivity, biocompatibility, and decreased cytotoxicity, it is crucial to optimise their surface characteristics [34]. As shown in Figure 4, different methods, including covalent and non-covalent ones, can be used to functionalize CNTs. For instance, the covalent technique of functionalization can be carried out through acid treatment, which encourages the addition of functional groups like carboxylic, hydroxyl, and carbonyl groups to the surface of CNTs. These functional groups can be used to further modify CNTs by adding various chemical or material components, such as chitosan [35].

Chitosan Modified Carbon and Non-carbon - based NANOPARTICLES

Among the several researched Nano systems, hollow porous non-carbon minerals are gaining more and more interest. Non-carbon minerals have several advantages for the separation process due to their active site delivery, high adsorption capacity, and porous structure. In both batch adsorption and adsorption-assisted Nano filtration procedures, the addition of non-carbon minerals to the membrane matrix results in extremely successful separations while in the periodic table, carbon can be thought of as a peculiar and enigmatic element. The term "carbon compounds" refers to a broad range of substances, including several petroleum chemicals, medicines, and polymers [36]. Carbon compounds, often known as carbon nanostructures, are a significant and distinct type of substances used in nanotechnology. With their distinctive physical and chemical characteristics, carbon nanostructures are crucial to the development of cutting-edge technologies.

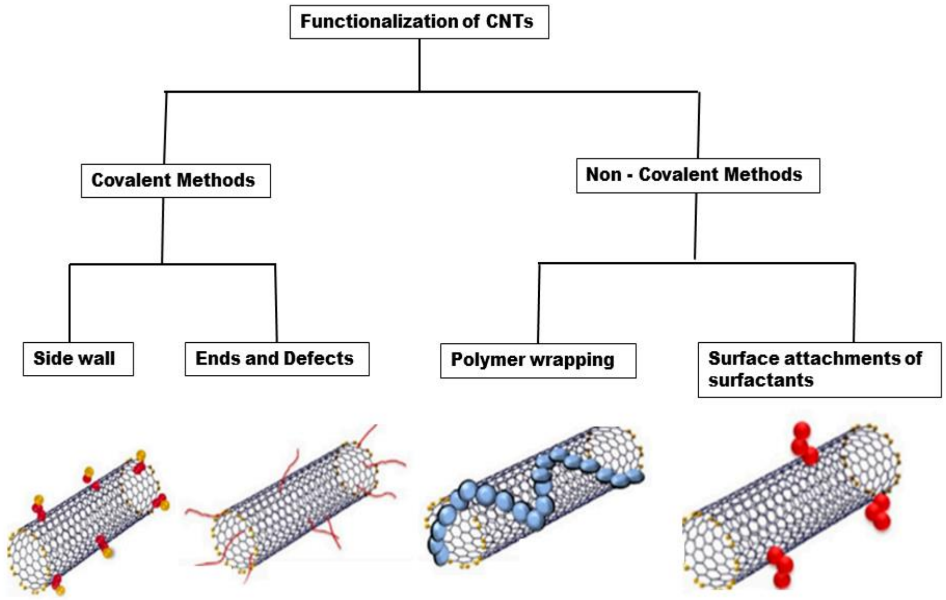

Figure 4. Method of Functionalization of Carbon nanotubes [22, 35].

Chitosan Modified with Metal - based Nanoparticles

Normally, it is assumed that metal-based NPs with adjustable size, shape, crystallinity, and functionality will enhance the membrane matrix's sorption properties. Two essential features of nanoparticles make them particularly desirable as sorbents. They have substantially bigger surface areas than bulk particles on a mass basis. To boost their affinity for target substances, nanoparticles can be functionalized with various chemical groups and classed as either organic or inorganic [37]. Drop-casting, one of the easiest and least expensive deposition methods, can also be used to create ordered thin-film or three-dimensional structures, depending on the functionalization or charges on the nanoparticle (NP) shells. However, it is rarely able to create homogeneous layers, especially on large surfaces, primarily because of different evaporation rates through the substrate or fluctuations in concentration, which can cause variations in the internal structure. Metal-based nanoparticles (NPs) are made of metals like gold and silver as well as metal oxides like Fe_3O_4 and ZnO. Permeability can be enhanced by metal-based NPs' high reactivity, empty orbital and coordination capacity, electrostatic interactions, and catalytic and oxidative functional characteristics [38]. These nanoparticles have been utilised to remove organic, microorganism, and heavy metal ions (chromium, mercury, and lead) from wastewater. However, the research has shown that employing these NPs as adsorbent materials on their own frequently leads to agglomeration and is not sustainable for the environment. Therefore, it is essential to immobilise these NPs onto a carbon nanomaterial or polymer matrix (chitosan) before using them to clean up the environment [10].

Chitosan Modified with Plant Extract

The method of producing nanoparticles using plant extracts as both capping and reducing agents is referred to as "green synthesis." Figure 5 shows the green synthesis of nanoparticles. The effectiveness of these resulting nanoparticles for biomedical purposes can be improved by utilizing plant extracts sourced from leaves, fruits, roots, and seeds. An extensive amount of research has been done to customise the properties of nanoparticles utilising a green synthesis strategy [6]. The creation of nanoparticles using green synthesis is shown in Figure 5. For the creation of gold (Au) nanoparticles. Virola oleifera exudate as a potential capping and stabilising agent. The introduction of capping agents was observed to shift the zeta potential of the synthesized Au nanoparticles from a negative charge to a positive charge on the particle surface [39]. Zhou and his colleague in 2015 generated a silver (Ag) nanoparticles using Rumex dantatus, Bergenia ciliata, Rumex hastatus, and Bergenia stracheyi as potential capping agents, resulting in Ag nanoparticles exhibiting robust antioxidant properties and minimal toxicity effects. Against six bacterial strains, the variously formed Ag nanoparticles demonstrated potent antibacterial action. The concentration of the synthesised nanoparticles rose along with their activity [40]. Green synthetic hematite was found to have anticancer, antibacterial, and antileishmanial properties. An example is created of hematite nanoparticles using Rhus punjabensis extract as a possible reducing agent. Additionally, the created nanoparticles significantly reduced the viability of HL-60 leukaemia and DU-145 prostate cancer cells [24, 31].

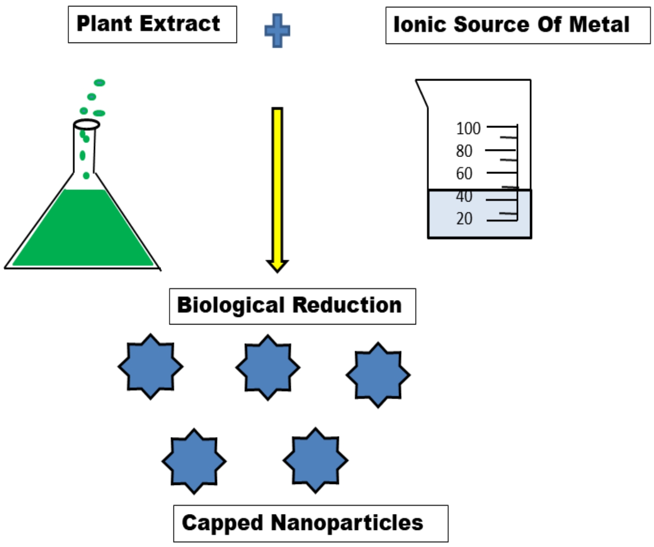

Figure 5. Green synthesis of Nanoparticles.

Chitosan Modified with Silver Nanoparticles

A growing number of people are using silver nanoparticles (AgNPs) because of their high stability and improved antibacterial properties. This may be a result of their compact size and high surface-to-volume ratio, which distinguishes them from their huge counterparts. Even at very low doses, they have been proven to exhibit potent antibacterial activity, even against resistant microbial strains. As a result, numerous techniques, including chemical, physical, photochemical, and biological ones, have been used to synthesise refined and recrystallized silver nanoparticles [41]. For instance, the chemical approach is the most popular way to create silver nanoparticles as shown in Figure 6, and it mostly consists of silver salt, stabiliser, and capping agent to regulate the growth of Ag-NPs. Due to its chemical stability and inexpensive cost, silver nitrate is one of these silver salts that is commonly employed [41, 42].

Chitosan Modified with Titanium Oxide Nanoparticles

Chitosan based Titanium Oxide nanoparticles (TiO_2) is environmentally safe and possesses superior photo catalytic and antibacterial capabilities, titanium dioxide, commonly known as titania, is frequently employed as a photo catalyst for environmental remediation. The three main phases of TiO_2 are rutile, anatase, and brookite, with anatase being the most advantageous of these. TiO_2 has been extensively examined, and prior research has indicated that TiO_2 nanoparticles have the capacity to degrade wastewater pollutants. TiO_2 is one of the Nano photo catalysts utilised in the treatment of wastewater. Nowadays, both chemical and physical techniques, including the hydrothermal, microwave, and sol-gel procedures, are used to create metal and metal oxide nanoparticles [43]. As can be seen in Figure 7, the sol-gel approach is the one most frequently utilised to create titanium dioxide out of all these synthesis methods.

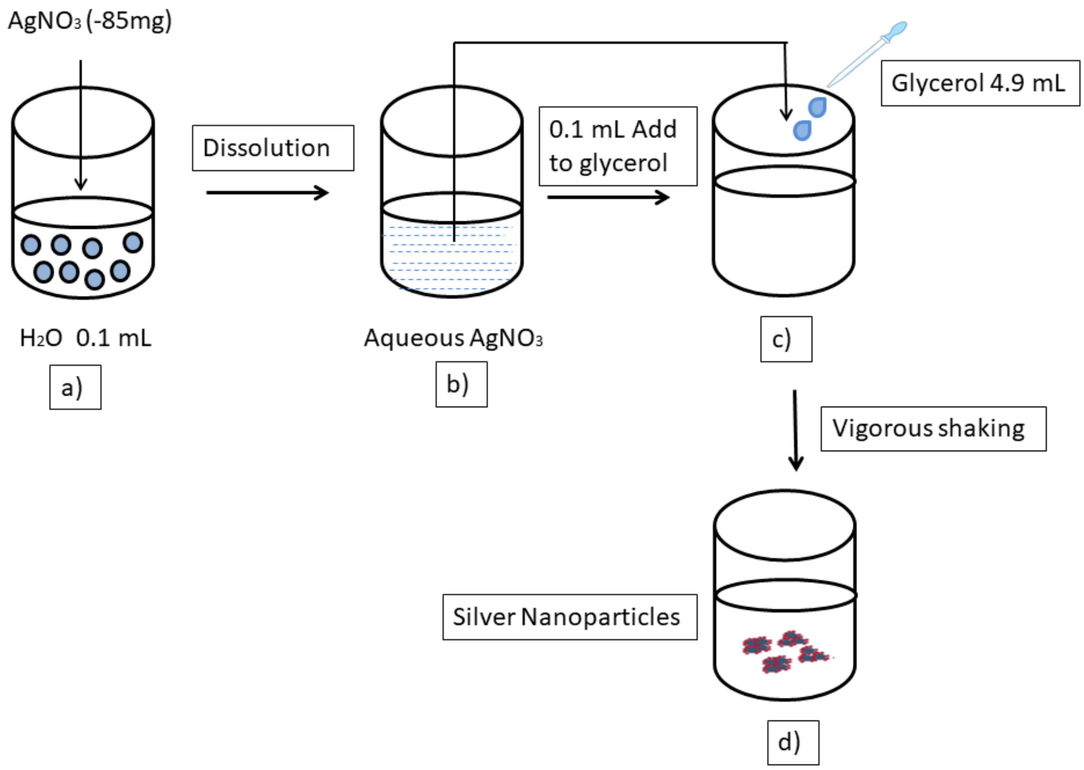

Figure 6. Chemical Synthesis of Silver nanoparticles (with $AgNO^3$ and Glycerol in natural condition).

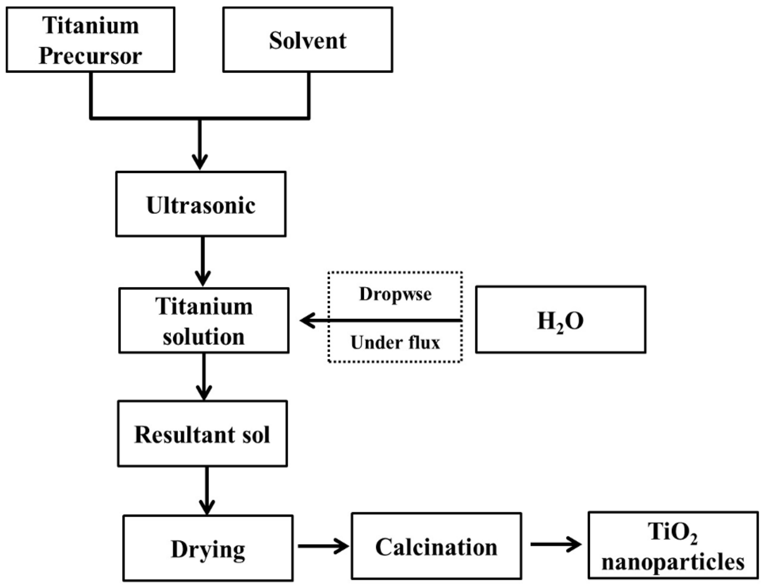

Figure 7. Schematic diagram of TiO_2 Nanoparticles formation.

APPLICATIONS

Environmental pollution is becoming one of the most important worldwide threats that humanity is facing, causing lasting damage. Continuous urbanisation and the rapid acceleration of industrialisation have upset the equilibrium of environmental composition by releasing hazardous materials, smoke, and other pollutants and poisonous fumes, which result in the toxic effects on living creatures [44]. Furthermore, overuse of natural resources owing to overcrowding, a huge number of automobiles, increased emissions of smoke from industry, and a variety of other things contribute to nature's devastation. This study will also encompass findings from isothermal investigations and delve into aspects such as the chemistry, morphology, manufacturing methodologies, and adsorption kinetics of chitosan-based membrane adsorbents. These membranes have been modified using various types of nano-materials, including metal-based, MOFs (Metal-Organic Frameworks), carbon-based, and non-carbon-based nanoparticles [45]. As they contaminate the environment, these substances pose a threat to ecology and human health, potentially contaminating soil, water, and air. This contamination can lead to adverse health effects, including conditions such as Alzheimer's, dementia, or hearing impairment. In the current circumstances, maintaining a clean and healthful water and air environment is of utmost importance [46]. However, while employing nanoparticles for environmental rehabilitation, researchers must ensure that they do not contribute to environmental damage. The majority of nano materials exhibit a propensity to cluster together, adhere to larger particles or surfaces, or potentially dissolve, resulting in the formation of toxic substances that pose environmental and human health risks. Nano materials, on the other hand, come into contact with their surroundings through their surfaces; as a result, nanoparticles may even be more harmful. Nanoparticles are typically functionalized to get over these restrictions and maintain their distinctive qualities, albeit the materials employed for functionalization have various effects on the physico-chemical characteristics of nanoparticles [47]. The fusion of nanoparticles and polymers within a single system has recently gained considerable traction in the realm of environmental remediation, particularly in the context of polymer functionalization of nanoparticles. Due to their outstanding and long-lasting mechanical strength, pore space, and surface qualities, polymer-coated nanoparticles are practical. Additionally, nanoparticles with polymer coatings maintain their natural properties and offer stability and biocompatibility, making them an improved surface coating [48]. Table 2 lists many kinds of polymer-functionalized nanoparticles that are employed in environmental remediation. These nanoparticles are target-specific and do not produce waste, thus there is no need to dispose of them after treatment. They also suggest a more environmentally friendly method of environmental remediation.

Heavy Metal Removal

Heavy metal pollution is a grave concern as it poses a significant threat to all living organisms. Presently, various methods, including bio adsorption, solvent extraction, phytoremediation with plants, microbial communities, hydrogel polymers for green separation, immobilization, and others, are under development for removing heavy metals from soil and wastewater. Considering that humans can ingest heavy metals through contaminated food, it is imperative to develop effective techniques to eliminate heavy toxic metals and their harmful effects in the air, soil, and water. Safeguarding human health from the serious risks associated with heavy metal exposure is paramount [49].

Chitosan nanoparticle is utilised as a flocculant in the treatment of water as well as in surfactants and membranes for evaporation, ultrafiltration, and reverse osmosis. Additionally, it is used to clean up industrial effluents that include heavy metal ions. The chitosan biopolymer has the ability to create complexes with transition metals [4]. These complexes involving heavy metals are established when heavy metal ions receive a donation of a nonbonding pair of electrons from nitrogen (-NH2) or oxygen (-OH) groups present in the chitosan structure. Chitosan granules made via tripolyphosphate-chitosan cross-linking show significant metal ion adsorption properties and might effectively be employed in wastewater treatment. The capacity of chitosan biopolymers to bind hazardous and heavy metal ions is one of their key applications. Zhang et al. reported the adsorption capacity values of modified chitosans (MChs) for the removal of metal ions [15]. It has been noted that the adsorption process depends on the process circumstances (pH, temperature, adsorbent dosage, contact time, co-existing ions), in addition to the adsorbent structure (modifications of chitosan). On several MChs, the following findings for Cu (II) ions adsorption were seen. The capacity of chitosan biopolymers to bind hazardous and heavy metal ions is one of their key applications. The modified chitosan's adsorption capacity values (MChs) for the elimination of metal ions were published by Zhang et al. [15]. The adsorption process has been observed to not be dependent on just on adsorbent structure (chitosan modifications), but additionally on process variables (pH, temperature, and adsorbent dosage). Researchers created monodisperse chitosan microspheres using the microfluidic technique and ran tests to investigate the adsorption properties to remove copper ions from waste water. The adsorption process was created using a variety of isotherms and kinetics models for adsorption [50]. The study's findings demonstrated a high adsorption capacity (75.52 mg/g) and a 74% readsorption efficiency after five cycles [34]. Density functional theory (DFT) analysis was used to investigate the adsorption capacity in the presence of competing ions. It was demonstrated that the core model, in which metal ions are co-ordinately coupled to a number of amino groups, is the most energetically advantageous structure among the examined metal complexes. A hybrid 3D printing technique for the bio adsorption removal of heavy metal ions was proposed in contrast to typical biosorbents, a 3D chitosan composite of a monolithic structure with reusable application was created for this purpose [38].

Recent information on the removal of lead (Pb), cadmium (Cd), mercury (Hg), and arsenic (As) by chitosan-based magnetic adsorbents from diverse aqueous solutions is reported in the paper. These adsorbents have been demonstrated to have a high adsorptive capacity toward hazardous metals and to be reusable in subsequent adsorption-desorption cycles. Chitosan nanoparticle (PP/SF/BF) composite materials were used as adsorbents in a study to remove cadmium ions from waste water. It has been proven that CS/SF/BF composite has a higher sorption capacity (419 mg/g) than PP/SF/BF composite (304 mg/g), which allows for multilayer adsorption. The results of the tests conducted indicate that the Freundlich isotherm best satisfied the adsorption process [51].

To remove Cr (VI) and Pb (II) ions from contaminated water, nitrogen-enriched chitosan-based activated carbon biosorbent was created. Thermodynamic parameters have been investigated, and a pseudo-second-order model accurately predicts the kinetics of the adsorption of these metal ions. This biosorbent can be used to treat wastewater due to its high efficacy, availability, recyclability, and cost-effectiveness [28, 50].

The researchers had studied successfully and synthesized a composite material known as Magnetic Phosphorylated Chitosan (P-MCS), which exhibited excellent adsorption capabilities for Co (II) ions, achieving an impressive adsorption capacity of 46.1 mg/g [21]. The adsorption behaviour of these ions was found to be in excellent agreement with the Langmuir adsorption isotherm model, indicating the formation of a monolayer of adsorbate molecules on the P-MCS surface. Furthermore, the kinetics of the adsorption process followed the pseudo-second-order model, suggesting a chemisorption mechanism. The conducted experiments provided compelling evidence that the Co (II) adsorption process primarily relies on the surface chelation between the functional groups of P-MCS and the metal ions [21, 32]. This highlights the potential utility of P-MCS as an effective adsorbent for the treatment of wastewater contaminated with Co (II) ions.

Through the synthesis of a cross-linked compound including carboxymethyl chitosan (CMC) and 2,3-dimethoxybenzaldehyde Schiff base, a very efficient adsorbent was created. This compound was created to purge aqueous solutions of heavy metal ions like lead (II) and cadmium (II). FTIR, XRD, and SEM investigations were used to fully characterise the synthesised material [7]. The research findings supported the Freundlich model, [52] which postulates a heterogeneous adsorption onto a non-uniform surface, as the adsorption process adherence. Additionally, the adsorption process kinetic behaviour closely followed the pseudo-second-order model, demonstrating the importance of chemical interactions in the adsorption mechanism [11, 52].

The creation of an eco-friendly chitosan-based nano adsorbent has been the focus of a unique and affordable method for water filtration. This method investigates the use of agricultural waste, inorganic nanomaterials, and polymer nanocomposite-based adsorbents to remove a variety of heavy metal ions from wastewater, including Hg (II), Cu (II), Cr (VI), Zn (II), Co (II), Cd (II), and Pb (II) [20].

Dye Degradation

Recalcitrant contaminants that are frequently detected in industrial effluents include nitroarenes, organic dyes, and solvents. Since these organic substances are poisonous to aquatic life, it is important that they are removed from aquatic systems. In terms of effectiveness, metallic nanoparticle-based remediation technologies outperform traditional techniques. Because they may form gel and have high affinity for metal cations, biopolymers like chitosan are regarded as appropriate support materials [16]. Palladium nanoparticle-based catalysis systems are effective at converting nitroarenes into aromatic amines by hydrogenation, dye molecule degradation, and the formation of C-C bonds in organic coupling processes. This work details the creation of a palladium catalyst supported by chitosan-carbon nanotubes as well as the outcomes of FTIR, XRD, TGA, and SEMEDX characterisation tests [19].

Herbicide Removal

The remediation of soil and water has been explored through the utilization of chitosan membranes, composites, and nanoparticles, as reported by Agostini de Moraes et al. in 2013, Carneiro et al. in 2015, and Celis et al. in 2012 [53]. Notably, De Moraes have identified the effectiveness of alginate and chitosan in removing herbicides.In their batch trial, three herbicides—diquat (DQ), difenzoquat (DF), and clomazone (CLO)—were investigated. Diquat (DQ) serves as a non-selective contact herbicide employed for weed and grass control in plantation crops. Difenzoquat (DF), a selective herbicide, is used to manage post-emergence wild oats in cereal crops. Clomazone (CLO) finds its application in rice fields to prevent the pre-emergence of both monocotyledonous and dicotyledonous plants [33, 37, 41]. Alginate (AG), chitosan (CS), and a mixture of both CS and AG were used to create three different types of membranes. The greatest method for getting rid of DQ and DF was discovered to be AG. Because AG contains carboxyl groups, there is coulomb's interaction between the positive charges of herbicides and the carboxyl groups. At concentrations between 50 and 200 M, it may adsorb 90% of DQ in 120 minutes. CS/AG membrane also shown significant DQ adsorption, however CS alone did not demonstrate removal. The findings suggest that the AG layer is responsible for all of the DQ adsorption on the CS/AG membrane [7, 54].

Bioaugmentation

Bioaugmentation is a technique used to enhance the ability of polluted soil to degrade contaminants by introducing specific consortia of microorganisms. Several factors influence the effectiveness of bioaugmentation, including the presence of contaminants and the physical and chemical characteristics of the soil. The critical factor is the selection of appropriate microorganisms that can competently coexist with the native microflora and efficiently degrade pollutants [54]. One strategy for improving bioaugmentation involves immobilizing microorganisms within various carriers or utilizing activated soil. Chitosan polymer has proven to be highly effective in immobilizing bacterial consortia when applied to soil. This can be achieved through various forms, such as composites, membrane flakes, or beads, allowing for a controlled and gradual release of bacteria into the soil it has proven to be a viable approach [55, 56].

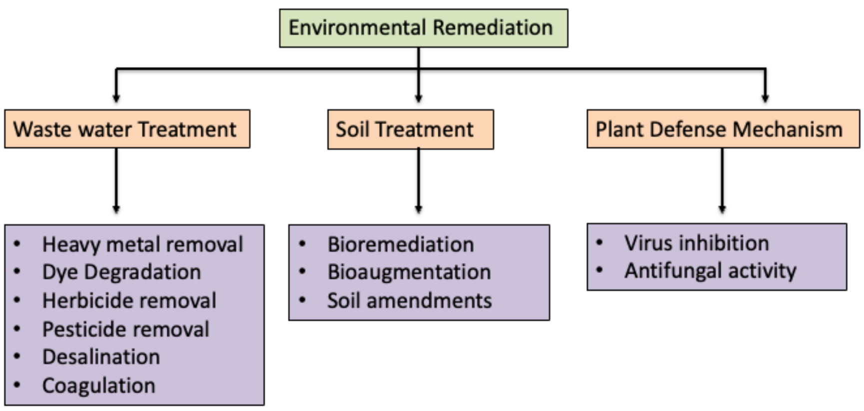

Figure 8. Applications of chitosan nanoparticle for environmental remediation.

Table 2. Nanoparticles with polymer caps used in remediation of the environment.

Nanoparticles	Capping agents	Principle	Substrate	Benefits
Ag	Core-shell magnetic chitosan	Adsorption	Cationic& anionic	Multi-dye adsorption, magnetic separation, and reusability
Ag	Chitosan	Catalysis	Methyl orange	Efficient and colour in visible dye
Ag & ZnO	PVP	Photocatalyst	Methylene blue	Efficient as compared to simple ZnO nanoparticles
Ag	PVA	Biosorption	Manganese ions	Immobilized on *Trichosporon cutaneum* R57 strain
Ag	Two different chitosan micro-particles	Adsorption	Methyl parathion (pesticide)	Efficient and reusable
Ag	Chitosan	Adsorption	Atrazine(pesticide)	Efficient and reusable
Ag & Au	Chitosan	Adsorption	Methyl parathion (pesticide)	Thermostable,highly hydrophillic
Au	PVP	Adsorption	Mercury	Efficiency can be controlled via optimizing the concentration of PVP
Fe	PVP	Catalytic adsorption	Bromate	Efficient and prolonged storage
Au	Chitosan	Sensor	Copper and Zinc ions	Detect even the lowest metal concentration
Magnetite	Chitosan & polythiophene	Adsorption	Mercury (II)	Efficient and sensitive
Silver tin sulfide	PEG	Catalyis	Eosin yellow& brilliant green dyes	Efficient, photostable, and recyclable
TiO_2	PVA	Photocatalysis	Rhodamine B	High efficient, stable,and reusable
Ag	PVA	Sensor	Hydrogen peroxide	Simple, cost-effective and reliable

This remediation technique can be applied both in-situ (at the contaminated site) and ex-situ (outside the contaminated area), and it is known for its swiftness and efficacy. In the research work of Zhang D, he utilized the fungus Absidia cylindrospora as a supplement for bioaugmentation in soil remediation [14]. Figure 8 shows the application of chitosan nanoparticle for environmental remediation while Table 2 shows the nanoparticles which is used in remediation of the environment.

FUTURE PERSPECTIVE AND CONCLUSION

This paper gives a complete overview of CS Nano composite and nano structured membrane adsorbent adsorptive applications, as well as an opportunity to grasp the benefits and downsides of incorporating different NPs (metal-based, carbonic, non-carbonic, MOF) into CS-based membranes. Chitosan has multiple natural benefits, including high porosity, biodegradability, structural integrity, and non-toxicity, according to several research. It has been established that modifying chitosan with nanoparticles improves its characteristics and applicability for a variety of applications. Functionalized chitosan-based composite materials (e.g., chitosan-based polymer Nano composites) in particular have received a lot of attention as potential adsorbents for dyes, oil spills, and heavy metal ions like cobalt, mercury, and copper. Furthermore, the combination of the separate components has resulted in these chitosan-based composite materials having excellent multifunctional characteristics. Because of the electron-rich functional groups on the polymer backbone, they have also been found to boost adsorption efficiency. In conclusion, these chitosan-based Nano composites, which were created by modifying functionalized chitosan with carbon nanostructured (carbon nanotubes) and nanoparticles (Ag, TiO_2ZnO, and S) demonstrated exceptional properties, making them strong candidates for environmental and wastewater remediation. There have been few investigations on the production of chitosan-based polymer Nano composites, primarily arising from the modification of chitosan with CNTs, TiO_2, Ag, ZnO, or S nanoparticles, for use in mercury remediation. As a result, it is strongly recommended that more research be done in this area.

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