Review on chitosan/copper composites as potential biocomposites for various applications

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ABSTRACT

Chitosan copper composites are a novel class of materials created by combining copper nanoparticles with chitosan, a biodegradable polymer derived from chitin. This composite synergizes the remarkable properties of both constituents, offering a wide array of potential applications. Chitosan contributes its biocompatibility, biodegradability, and versatile binding capabilities, while copper nanoparticles add antimicrobial, electrical, and catalytic properties. This composite's synthesis methods, including solution blending and in-situ reduction, are detailed, highlighting their influence on final properties. As an innovative convergence of biopolymers and nanomaterials, chitosan copper composites present a promising avenue for developing advanced materials with diverse applications.

Keywords— chitosan; biocomposite; copper coating; nano-materials

I. INTRODUCTION

Nanotechnology is the study of smaller particle materials with dimensions ranging from 1 to 100 nm, which provides unique features of materials utilized for specialized applications [1]. A composite is a multiphase material that exhibits significant amount of each constituent phase's qualities, providing better combination of properties in such a way that better property combinations are created by the careful combining of two or more unique materials [2]. Nanocomposites (NC) are multiphase materials with nanoscale modifications in one of the phases. The definition of nano-composite material has grown substantially over the years to include a wide range of systems, including one-dimensional, two-dimensional, three-dimensional, and amorphous materials comprised of distinctly dissimilar components which are blended at the nanoscale scale. They were originally reported on 1950 followed by the studies of polyamide nanocomposites in 1976. However, they were not widely explored in both academic and industry facilities until Toyota researchers launched a systematic analysis of polymer/layered silicate clay material composites in the early 1980s and later becoming the most utilized material [3-4]. According to Azonano (2009), nanocomposites are "materials with a nanoscale structure that improve the macroscopic properties of products." He discovered that nanocomposites are often made of carbon, clay, polymer, or a mixture of these components using nanoparticle building blocks [5]. They are likely to have novel properties as a result of the fusion of each component. Due to its mechanical, solvent-resistant, superior thermal, and fire-retardant qualities, NC has gained popularity in recent years [6]. The particle size and distribution, surface features, geometric shape, and dispersion state can all have a major impact on composite qualities. Now a days, polymer nano-composites are becoming more popular as a result of the current commercial accessibility of nano-particles [7]. Recently, advances in the ability to characterize, produce and manipulate nano meter-scale materials have led to their increased use as fillers in new types of nano-composites.

1. Classification

Nanocomposites can be classified into various categories based on the materials incorporated, dimensions of the framework, types of reinforcement material, and synthetic approach. The commonly observed fillers used in nanocomposites are shown in Figure 1.

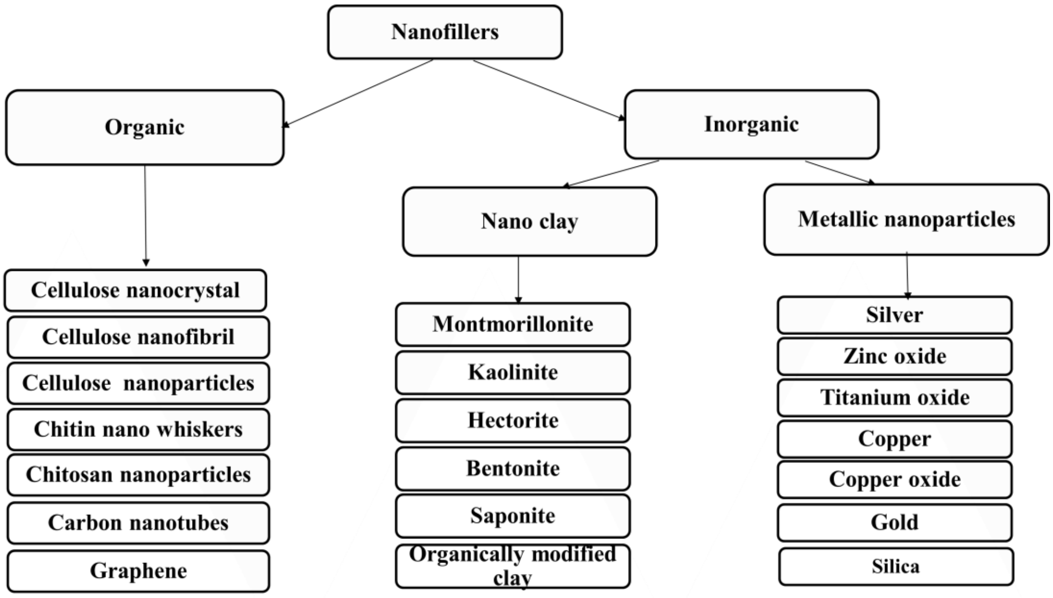

Figure 1: Fillers used for the preparation of nano-composites

Nanocomposites, a class of materials formed by integrating nanoparticles into a matrix, have emerged as a revolutionary area of research with diverse applications across scientific, industrial, and technological domains. The controlled manipulation of materials at the nanoscale imparts novel properties and functionalities, often surpassing those of their individual components. Among the intriguing array of nanocomposites, chitosan-copper nanocomposites stand out as a remarkable example of synergistic material engineering, combining the inherent strengths of chitosan and copper nanoparticles. This review delves into the synthesis methods, properties, and wide-ranging applications of chitosan-copper nanocomposites, underscoring their significance in various fields.

2. Properties of copper and chitosan as an antimicrobial agent

The fusion of biopolymers and metals has emerged as a groundbreaking innovation with far-reaching implications across diverse industries. This convergence brings together the versatility of biopolymers, derived from renewable natural sources, and the unique properties of metal nanoparticles, often at the nanoscale, to create a new class of materials that transcends the capabilities of their individual components. The importance of biopolymer and metal composites spans numerous fields, from medicine to electronics, environmental remediation, and beyond. Biopolymers, such as chitosan, cellulose, and starch, embody sustainability. Sourced from renewable materials, they present a greener alternative to synthetic polymers. Chitosan is a natural, biodegradable, and cost-effective biopolymer. Chitosan possesses intriguing antimicrobial properties [8]. As a result, chitosan is commonly employed in antibacterial applications due to its antibacterial activities against gram-positive bacteria, gram-negative bacteria, and fungi [9]. Chitosan has piqued the interest of researchers as a nano-composite matrix due to its novel features for a variety of applications. Integrating them with metal nanoparticles, like silver, gold, copper enhances their functionalities, creating materials that are not only environmentally friendly but also biocompatible. The antibacterial capabilities of copper were used by ancient cultures long before the nineteenth century when the idea of germs was first defined. Cu has the intrinsic ability to kill germs when it comes into touch with them [10-12]. In-depth research has been done on the molecular mechanisms behind copper's antibacterial effects. Additionally, researchers are demonstrating the inherent ability of copper alloy "touch surfaces" to eliminate a variety of germs that pose a concern to public health [13]. Victor Burq conducted considerable study to support his discovery that in 1852 that those who worked with copper experienced far fewer cholera mortality than anyone else. He submitted his research to the French Academies of Science and Medicine in 1867, telling them that applying copper to the skin could help prevent cholera [14].An extensive variety of bacteria can be eliminated by copper alloy surfaces naturally. There have been a lot of peer-reviewed antimicrobial efficacy studies on copper's ability to kill E. coli O157:H7, methicillin-resistant Staphylococcus aureus (MRSA), Staphylococcus, Clostridium difficile, influenza A virus, adenovirus, and fungi over the past ten years. These studies have been done in the interest of preserving public health, especially in healthcare settings with their susceptible patient populations [15]. A variety of studies have been conducted in this area during the past several years.

Arun et al. studied the mechanical characteristics of the electrodeposited copper thin film; deposited on double zincated aluminium, such as scratch resistance and microhardness.The size of the copper coating's crystallites was used to quantify the coating's scratch and microhardness and to correlate those values. With the decrease of crystallite size, it was discovered that both characteristic values increased. Using the colony count method, the coated sample's antimicrobial effectiveness was assessed against Escherichia coli bacteria and compared to that of commercially available bulk copper. After six hours of exposure to the copper-coated surface, 94% of E. coli cells had died [17].The maximum strength of nanotwinned copper samples with varying twin thicknesses was examined by Liu et al. By using the electrodeposition process, 99.99% pure copper thin film with nanocrystalline size can be easily produced on the aluminium touch surface [18]. Neo et al. effectively created a super hydrophilic surface by electrolytic plasma oxidation of aluminium (Al) followed by Cu-dotted electroplating. E. coli ATCC 25922, methicillin-resistant Staphylococcus aureus (MRSA) ATCC 43300, and vancomycin-resistant Enterococcus faecium (VRE) ATCC 51299 were all killed by the Cu plate and Cu-dotted oxide surfaces. It was discovered that the super hydrophilic Cu-dotted oxide coating surface provides an excellent technique for suppressing bacterial growth and survival on contact surfaces, lowering the danger of infection and disease spread, particularly in moist or wet conditions. [19]. Using the electrodeposition technique, a copper thin film was created on double zincated aluminium. The crystalline size has a direct impact on the coating's surface energy. Surface shape, in addition to surface energy, plays an important effect in surface wettability. The coating shape and crystallite size alter as the electrodeposition current density (j) changes [20].

By utilizing electrodeposition in a non-cyanide alkaline bath, Arun et al. effectively explored the copper coating on the aluminium surface. Before copper is deposited, the substrate has been pre-zincated to ensure strong adherence. It is discovered that the Williamson-Hall method's strain energy calculation shows an increase. Additionally, studies on the wettability of double-distilled water with respect to the electrodeposited copper coatings that are coated at various current densities are conducted. The coating is more water-wettable at greater current densities because, under these circumstances, the coating's grain size is reduced, and its shape changes to a more advantageous dense nodularity [21]. In order to treat the E. coli ATCC 25922 culture with 99.99% pure copper thin film, which is created by the electrodeposition method, Arun et al. explored the mode of attack of copper ions on microorganisms. Analysis has been done on the morphological alterations and the structural changes of the cell in E. coli cells. Studies using electron microscopy showed that copper-treated E. coli cells had more wrinkling and damage than untreated ones. This is because the lesions that the copper ions cause a large number of ions and amino acids to inflow and efflux [22]. This biocompatibility is paramount in medical applications, where the potential for reduced toxicity and adverse effects makes biopolymer-metal composites ideal candidates for implants, drug delivery, wound healing and potential materials for touch surfaces. Various methods for the preparation of chitosan/copper composites are shown in Table 1.

Table 1: Applications of chitosan/copper nanocomposites

Sl no	**System**	**Method of preparation**	**Applications**
1	chitosan-copper (CS-Cu) nanocomposite	Synthesized without the aid of any external chemical-reducing agents.	Photocatalyst Antimicrobial agent Anticancer agent [23]
2	chitosan-based copper nanocomposite (CCNC),	mixing chitosan and copper nanoparticles.	Wound healing [24]
3	cuprous oxide/chitosan nanocomposites	electrochemical deposition	Photocatalyst for degradation of Brilliant red X-3B [25]
4	CuO/chitosan nanospheres	straightforward wet chemical procedure	Photocatalyst for destruction of organic pollutants [26]
5	Chitosan (ChdSb)/copper oxide (CuO) nanoparticles		Photocatalyst [27]
6	Cu_2O/crosslinked-chitosan nanocomposites (Cu_2O/CS NCs)	straightforward liquid phase precipitation-	Photocatalyst for decolorization of dye X-

		reduction	3B [28]
7	Chitosan (CS) attached copper oxide (CuO)	chemical precipitation process	Photocatalyst for Methylene blue (MB) dye degradation, Antibacterial agent [29]
8	Chitosan base copper oxide (CH-CuO) nanoparticles	environmentally friendly production	Photocatalyst, Antibacterial agent [30]
10	Copper oxide nanoparticles (CS-CuO nanocomposite)	Eco-friendly production	Antibacterial agent [31]
11	Water-dispersible chitosan nanoparticles loaded with mixed valence copper	hydrothermal (HT) approach	Antibacterial agent [32]
12	Copper nanoparticles (NpCu) with chitosan matrix	Green synthesis	Antibacterial agent [33]
13	Cu@Chitnanocomposite	Metal-vapor synthesis (MVS)	Antifungal agent [34]

3. Chitosan- Copper nanocomposites

Chitosan/nCu is frequently utilised to improve healing or infection control, with particular emphasis on the antibacterial mode of action and toxicity [35]. Anu et al. created a chitosan-based copper nanocomposite (CCNC) by combining chitosan with copper nanoparticles. In an open excision wound model in adult Wistar rats, CCNC was applied externally to measure its wound healing capability and to explore its effects on some essential components of the healing process. Wound contraction was significantly increased in the CCNC-treated animals. It was discovered that a chitosan-based copper nanocomposite effectively promoted cutaneous wound healing by modulating numerous cells, cytokines, and growth factors at various stages of the healing process. Figure 2 illustrates a potential CCNC healing mechanism [36]. Further studies shows that adding copper to wound dressings would improve wound healing. When wound dressings containing copper oxide were applied to wounds inflicted on genetically engineered diabetic mice (C57BL/KsOlaHsdLeprdb), they increased gene and in situ up-regulation of proangiogenic factors, blood vessel formation, and wound closure when compared to control dressings (without copper) or commercial wound dressings containing silver. This research demonstrates the ability of copper oxide-containing wound dressings to promote wound healing and gives information on the molecular mechanisms by which copper oxide-impregnated dressings promote wound healing [37]. Chitosan-copper (CS-Cu) nanocomposite was found to be an effective antibacterial agent against Gram-positive and Gram-negative bacteria, as well as fungi. The innovative substance was used in biological applications such as the production of drug-resistant antimicrobials and anticancer medicines [23]. To enhance the antibacterial capabilities and corrosion resistance of the substrate, the coating of chitosan-copper nanocomposite on stainless steel 316L using electrophoretic deposition was conducted by varying concentrations of Cu nanoparticles after the in-situ synthesis of Cu nanoparticles modified by chitosan. Several Gram-positive and Gram-negative microorganisms were used to examine the antibacterial effects of nanocomposite coatings. Results showed that the antibacterial activity and corrosion resistance of 316L stainless steel substrates were significantly improved [25]. The first eco-friendly bio-inspired chitosan/copper oxide (CS-CuO) nanocomposite utilising rutin was developed and has been developed as a potential anticancer drug [38]. To create chitosan/copper nanocomposites (CS/Cu-NCs) and chitosan/polyacrylic acid/copper hydrogel nanocomposites (CS/PAA/Cu-HNCs), varied concentrations of copper were loaded onto the produced NPs. Investigations were conducted on the produced materials' antibacterial efficacy towards bacteria, fungus, and yeast. The findings showed that CS/PAA/Cu-HNCs had higher swelling percentage and copper release than CS/Cu-NCs [39].

Sun et al. prepared chitosan-copper-gallic acid nanocomposites (CS-Cu-GA NCs) using microwave-assisted techniques. Chitosan, Cu NPs, and Cu^{2+} all have built-in antibacterial capabilities that are combined in CS-Cu-GA NCs. Animal studies showed that the antibacterial treatment containing CS-Cu-GA NCs effectively promoted the healing of wounds infected with S. aureus while causing no harm to healthy tissues. Additionally, a bandage with superior water swelling and antibacterial properties was created using the antimicrobial dressing [40]. The green synthesis method was an environmentally benign way to create physiologically active copper oxide nanoparticles from Ficus carica leaf extract. The antibacterial activity of copper nanoparticles and chitosan alone was found to be less than that of the Cu-chitosan nanoparticle composite, indicating that the antibacterial activity of CuO NPs is greatly enhanced by the addition of chitosan stabiliser [41]. Staphylococcus aurous, a Gram-positive bacteria, and Escherichia coli, a Gram-negative bacteria, were used to test the antimicrobial activity of produced fabric samples treated with chitosan nanoparticles and CuO/chitosan nanocomposites. The type of coating material, which is determined by the degree of improvement in the % RBC of both Gram-positive and Gram-negative bacteria, follows the following descending order: fabric coated with CuO/chitosan nanocomposite > fabric coated with chitosan nanoparticles > none. It is obvious that the higher percent RBC results refer to the treated fabric samples' enhanced antibacterial activity [42].

By using in situ reduction of Cu(II) to immobilise copper nanoparticles on the amino-enriched surface of chitosan (CTS), Miao et al. created L-ascorbic acid-stabilized Cu-CTS nanocomposites. The average size of the copper nanoparticles was (2.6 ±0.5) nm. It was discovered that the Cu-CTS nanocomposites exhibited a broad antibacterial range and high antimicrobial activity against the fungus Monilia albican and the Gram-positive bacterial pathogen Staphylococcus aureus [43]. Umoren et al. created the chitosan-copper oxide (CHT-CuO) nanocomposite using $CuSO_4 .5H_2O$ as a precursor and olive leaf extract (OLE) as a reducing agent. By using the cup plating or disc diffusion methods, the antibacterial activity of the synthesized nanocomposites was assessed against Gram-positive and Gram-negative species.Escherichia coli, Pseudomonas aeruginosa, Pseudomonas, citronellolis, Bradyrhizobium japonicum Kliebisella sp., , and Ralstonia pickettii are examples of gram-negative bacteria. Staphylococcus haemolytica, Bacillus cereus, and Micrococcus luteus are examples of gram-positive bacteria that were used for this test. As-Synthesized CHT-CuO nanocomposite demonstrates encouraging antimicrobial properties and may be used as an antibacterial agent in packaging and medical applications [44].

4. Chitosan-copper nanocomposite hydrogel

Copper nanoparticles were created by Jayaramadu et al. utilising the precipitation process and a pseudonatural cationic chitosan biopolymer as a stabilising agent. Solution casting was used to create the nanocomposite hydrogels from the produced nanoparticles in a 1:1 blend of chitosan and pluronic F127 polymer solution. Through an inhibition zone method, the created nanocomposite hydrogels were evaluated for their antibacterial efficacy against the gram-positive and gram-negative bacteria S. aureus and E. coli. The findings demonstrated that the copper-embedded chitosan-pluronic F127 nanocomposite hydrogels may be utilized successfully for both wound care and antibacterial applications [45]. Metal vapour synthesis (MVS) was used to create copper-chitosan nanocomposite-based chitosan hydrogels (Cu-Chit/NCs hydrogel).Study demonstrates the antifungal activity of Cu-Chit/NCs hydrogels against aflatoxigenic strains of A. flavus and demonstrates that, depending on the kind of fungal strain and nanocomposite concentration, the antifungal activity of nanocomposites in vitro can be successful.Cu-Chit/NCs hydrogels, which have the ability to either increase or reduce particular types of proteins, were used to treat A. flavus. In studied isolates, Cu-Chit/NCs hydrogel reduces the impact of G6DP isozyme without changing the activity of peroxidase isozymes [46]. By adding the Cu^{2+} ions to a hydrogel made of chitosan, Vanashi et al. created a copper-containing hydrogel (Cu/CH).For the formation of the hydroxyl radical, a catalytic mechanism was suggested. The research on reusability revealed that Cu/CH can be recycled multiple times without losing its catalytic activity. The performance of various metal ions injected into the hydrogel in the generation of hydroxyl radical was also examined [47]. Paul et al. concentrate on creating a topical administration system for a greenly synthesized copper oxide nanocomposite gel. In order to treat human diseases, the healthcare sector is under a lot of strain and requires unique, multifunctional materials. The most innovative materials now used in the medical field are biopolymers covered with nanocomposites. The CS-CuO nanocomposite gel that was created possesses antibacterial qualities and works well when applied topically [48].

5. Chitosan-copper beads

Using sodium tripolyphosphate as the cross-linker, Sana et al. synthesized CuO nanoparticles in situ during the development of physically cross-linked chitosan hydrogel beads. This study looked into the possibility of using these nanocomposite beads for drug delivery applications. Against Escherichia coli and Staphylococcus aureus bacteria, the nanocomposite hydrogels showed good antibacterial properties [49]. Copper chitosan composites represent a promising and innovative class of materials with a wide range of potential applications. Through the synergistic combination of chitosan's biocompatibility and copper's antimicrobial properties, these composites offer unique advantages in various fields such as biomedicine, environmental remediation, and food preservation. The incorporation of copper into chitosan matrices enhances their antimicrobial efficacy, making them effective agents against a broad spectrum of pathogens. This is particularly valuable in medical applications where reducing the risk of infections is critical, as well as in water treatment systems where the removal of harmful microorganisms is essential for maintaining water quality.

II CONCLUSIONS

The versatile nature of copper chitosan composites allows for their adaptation into different forms, such as films, membranes, coatings, and nanoparticles, thereby enabling their use in diverse scenarios. Their biodegradability and reduced environmental impact compared to traditional antimicrobial agents also contribute to their attractiveness from a sustainability standpoint. However, challenges still remain in terms of optimizing the composite's properties, ensuring consistent performance, and addressing potential cytotoxicity concerns. Further research is needed to thoroughly understand the long-term stability, release kinetics, and interactions of these composites with various environments. In the coming years, as research and development in the field of materials science progress, copper chitosan composites are likely to play a pivotal role in revolutionizing multiple industries, offering innovative solutions to address microbial contamination, infection control, and environmental preservation. Continued efforts in advancing their formulation, synthesis techniques, and application methods will unlock their full potential, leading to a safer and healthier future.

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