Synthesis and Characterization of Copper Nanoparticles Incorporated Chitosan-Spider Web Biopolymer Blend

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ABSTRACT

Chitosan is a biopolymer obtained from deacetylation of the natural chitin polymer, one of the most abundant and renewable material on Earth. Due to its unique macromolecular structure, distinctive physical and chemical properties, biological activities, and versatility, chitosan, a natural biopolymer, has attracted considerable attention in fundamental science, applied research and industrial biotechnology. The synthesis of copper nanoparticle incorporated chitosan-spider web (Ccob-CuNPs) blend as a biopolymer blend was carried out in this study. The chitosan and spider web composite were synthesized by blending the two biopolymer solutions in various ratios **5**:**1**-**5**:**5** chitosan/spider web blend (with varying the concentration of the spider web solution) to note which concentration will suitably enhance molecular structure of the chitosan biopolymer which was monitored using the FTIR spectrophotometer. Copper nanoparticles was also synthesized by mixing a $CuSO_4$ solution with a solution of ascorbic acid and centrifuged using Fischer centrifuge (model **208**) with a rmp of **3400** for **15** minutes to further separate the nanoparticles. In the order to obtain the desired Ccob-CuNPs blend, the synthesized biocomposite (chitosan-spider web) was reacted with the synthesized copper nanoparticles by simple stirring with the aid of a magnetic stirrer. This mixture was further subjected to various characterizations such as UV spectroscopy, FTIR spectroscopy and XRD to identify their specific properties. The UV results of the formulated blend (Ccob-CuNPs) at the different blending ratios showed a maximum absorption band at the wavelengths ranging from **200**-**300** nm. The interaction between the biocomposite and the synthesized nanoparticles was studied using Fourier transform infrared (FTIR) spectroscopy, which showed the formation of new vibration band at **2467.5** cm^{-1} corresponding to the C-M bond, implying the capping of the nanoparticles by the biocomposite. The average size of the Ccob-CuNPs was estimated to be **57.8** nm using X-ray diffraction (XRD) analysis. These findings completely confirmed the synthesis of CuNPs through a biocomposite medium.

Keywords: Chitosan-spider web, copper-nanoparticles, biopolymer, UV, FTIR and XRD.

INTRODUCTION

Polymers have existed in natural form since life started. These biological macromolecules, including DNA, proteins, RNA, and polysaccharides, are essential for the functioning and survival of both plant and animal organisms. Humans have utilized naturally occurring polymers as materials to provide basic requirements such as clothing, decoration, shelter, tools, weapons, writing materials, etc.[1]

Among the various types of polymers, biopolymers have created renewed interest in the scientific world.[2] Biopolymers (defined as "polymers that involve living organisms in their synthesis process") are derived from organic substances found in nature including wood, vegetation, crustacean exoskeletons, fungi, and similar materials. Biopolymers represent a specific class of materials among polymers based on natural

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resources.[3] These occur in nature as macromolecules. Common examples of such polymers include cellulose, hemicelluloses, lignin, silk, and starch. Biodegradable biopolymers (BDPs) are an alternative to petroleum-based polymers.[1] Besides BDP biodegradability, other aspects relevant for processing are also important, i.e., thermal stability and viscosity that allow the use of conventional technologies and machines without large adaptations.[1] The economic value of renewable raw materials will increase to a significant extent and stimulate new industrial activities.[4]

Chitosan is a biopolymer obtained from deacetylation of the natural chitin polymer, one of the most abundant and renewable material on Earth.[5] Deacetylation process is a process of hydrolysis of acetamide groups in chitin using strong NaOH solution at high temperatures (**100** ℃ or more) produces the amino group of the new compounds (chitosan). The number of amino groups formed will affect the properties of chitosan.

Chitin serves as a key structural element in several biological contexts, including fungal cell walls, arthropod exoskeletons (such as those of crabs, lobsters, shrimp, and insects), mollusk radulae, cephalopod beaks, and fish scales.[6] Henri Braconnot is credited with the discovery of chitin in 1811, while Charles Rouget's work in 1859 marked the beginning of chitosan research. The term 'chitosan' was later introduced by Felix Hoppe Seyler in 1894.[7] Chitosan's unique macromolecular structure, combined with its biocompatibility, biodegradability, and other beneficial properties, has garnered significant scientific and industrial attention since the late 1970s.[8] Its widespread availability allows for the extraction of over 1000 tons annually, with approximately 70% sourced from marine organisms.[9]

Due to its distinctive macromolecular structure, unique physical and chemical characteristics, biological activities, and versatility—qualities that differentiate it from synthetic polymers—chitosan has become a focal point in fundamental scientific research, applied research and industrial biotechnology.[6] In addition to its biodegradability and biocompatibility, it has many reactive amino side groups that offer the possibilities of chemical modification and formation of a large variety of beneficial derivatives.[10]

Spider silks exhibit a range of unique biomechanical properties, coupled with biocompatibility and slow degradation, making them promising materials for investigation as biomaterials in tissue engineering and guided tissue repair applications and drug delivery, for cosmetic products (e.g., nail and hair strengthener, skin care products) and industrial materials (e.g., nanowires, nanofibers, surface coatings)[11,12] and this significant importance will be employed to the improvement of chitosan since the presence of hydroxyl functionality catalyzes its inherent disposition to swell in the presence of water and makes it challenging for thin film studies (among others) to be carried out using it as a matrix.[13] In a bid to overcome these challenges, scientists have adapted approaches like copolymerization and grafting in order to stiffen and restrict the swelling potential, amongst other target goals.[13]

Polymer blends are frequently used in the food-packaging industry to: improve the processability of a natural polymer to suit the industrial applications; improve the physical, chemical, and mechanical properties of the biodegradable material; and adapt to frequent changes in demand for new materials for the food-packaging industry.[14] In comparison to copolymerization, polymer blends offer a low-cost process and instead of complicated chemical processes, simple physical processes are involved to achieve the desired characteristics.[15] The factors that determine the performance of polymer blends are morphology, miscibility, and compatibility.[16] The morphology of the immiscible polymer blends is determined by several parameters such as the concentration of the blended materials, viscosity ratio, compatibility between the blend polymers, and interfacial tension between the polymers.[16]

The synthesis of copper nanoparticles (Cu-NPs) in particular has garnered more attention than that of other NPs due to their practical qualities, which may be obtained at a significantly lower price than that of silver and gold.[17] NP synthesis in polymer media has shown promise because of its solubility, ease of processing, low toxicity, and potential to control the growth of the final nanoparticles.[18]

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Due to their accessibility, biocompatibility, and low toxicity, bio-polymers are increasingly being used as stabilizers in the production of Cu-NPs.[19]

Chitosan

Chitosan, a sugar-like substance, is derived from the exoskeletons of shellfish, such as crabs, lobsters, and shrimp. It finds use in medicine and pharmaceutical production. Chitosan is a fibrous material with the potential to reduce the absorption of fats and cholesterol in the body. It also helps blood clot when applied to wounds.[20]

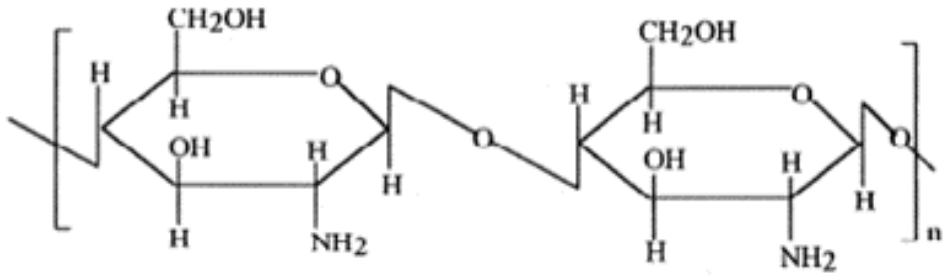

Fig 1: Structure of chitosan

Chitosan as a Biomaterial

Chitosan is obtained through the deacetylation of chitin, which is one of the most abundant biomaterials after cellulose.[10] This one is a polysaccharide which can be found in crustaceans, insects, or fungi (Table **1**).[24] Chitin is considered a linear long-chain homopolymer which is composed of N-acetyl glucosamine, and can develop three polymorphic forms known as α-, β-, and γ-chitin.[21]

Commercial chitosan (Figure **1**) is made up of D-glucosamine and N-acetyl glucosamine and is gotten from the partial deacetylation of chitin[22] which changes acetamido groups into amino groups. There are three kinds of this biopolymer depending on its molecular weight: low molecular weight, high molecular weight, and oligochitosans.[23]

Table 1: Some of the main chitin sources and percentages.[24]

Source	**Percentage (%)**
Shrimps	**30**–**40**%
Squids	**20**–**40**%
Krill	**20**–**30**%
Crabs	**15**–**30**%
Fungi	**10**–**25**%
Insects	**5**–**25**%
Oysters	**3**–**6**%
Clams	**3**–**6**%

Spider Silk as a Biological Polymer

Silks are protein-based fibers, produced by several insects including silkworms and spiders.[25] Spider silk has been investigated for decades due to the intriguing mechanical properties.[26] It's low or zero immune-reactivity, the absence of toxicity, and slow biodegradability when in contact with the human body, also make silk an attractive biomaterial.[27] Silk is a fibrous material that exhibits extremely high strength and toughness with regard to its low density. For textile applications, silk from the larvae of the moth Bombyx

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mori (silkworms) is processed on a large scale in silkworm farms.[28] Of note, many spider silks have better mechanical properties than silkworm's silk.[29] The different properties are due to the different natural functions of the material. Silkworms use their silk for protection during their metamorphosis, while many spiders use silk to catch prey.[25]

Spider silks have been a focus of research for almost two decades due to their outstanding mechanical and biophysical properties.[30] Recent advances in genetic engineering have led to the synthesis of recombinant spider silks, thus helping to unravel a fundamental understanding of structure–function–property relationships.[31] Nature has evolved a range of materials that compete with man-made materials in physical properties; one of these is spider silk.[31]

Fig 2: An image of spider web.

Diverse uses of *Araneae* silks originate from the outstanding physical properties that are tailored for specific needs, resulting in variation of mechanical properties.[32] In these terms, high-tech fibers appear to be more brittle compared to the more extensible dragline threads, making spider dragline silks the strongest material.[33] In addition to this, spider dragline silks are light-weight materials that can undergo super contraction when hydrated.[33]

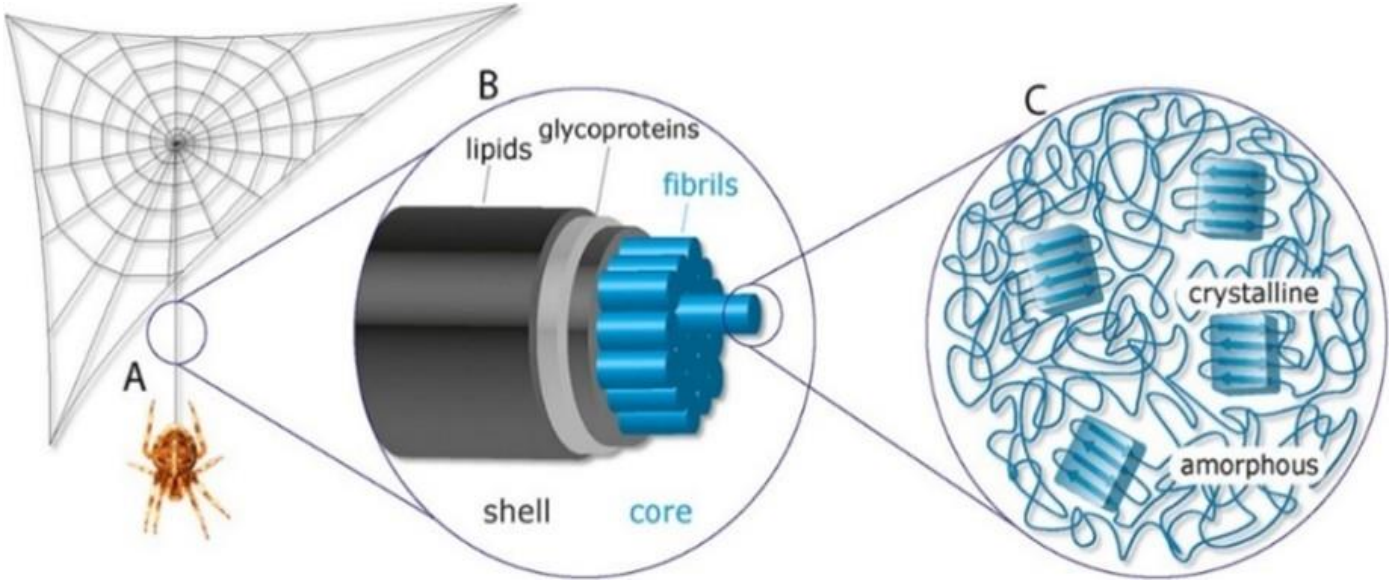

Figure 3: Schematic display of spider silk.

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General Properties of Spider Silk

Spider silk is a semi-crystalline biopolymer with a unique combination of high tensile strength, high elasticity and high modulus.[34] The 0.2–1.0 mm diameter silk fibres have a higher breaking energy than other natural or synthetic fibrous polymers, far exceeding that of high tensile steel and Kevlar on a weight-for-weight basis.[35] Spider silk's unique combination of strength and elasticity is judged to be superior to that of synthetic high-tech fibres made of polyamide or polyester.[36] As well as being five times stronger than steel on a weight-by-weight basis, spider silk is finer than human hair, more resilient than any synthetic fibre, and completely biodegradable.[36] Spider silk is shown to possess strength as high as 1.75 GPa at a breaking elongation of over 26%. It is three times tougher than aramid and other industrial fibres.[36] Compared to silkworm silk, it is more waterproof and can absorb three times the impact force without breaking. All these properties are achieved in a fibre produced in ambient temperatures, low pressure and with water as a solvent.[36]

Copper Nanoparticles

The rapid progress in nanotechnology has positioned nanoscience as a prominent area of research, making it one of the most studied scientific fields over the past twenty years.[37] Generally, nanoparticles (NPs) are characterized by diameters of 0.1 μm (100 nm) or smaller, with specific properties largely dependent on their size.[37] The allure of NP research stems from their exceptional properties compared to their bulk counterparts, leading to their diverse applications across various fields. These properties include catalytic, thermal, electrical conductivity, optical, and biological functionalities.[39] Their advantageous attributes are driven by their high surface energy, large surface area to volume ratio, and diminutive sizes.[40]

The synthesis of copper nanoparticles (Cu-NPs) has garnered more attention compared to the synthesis of other nanoparticles due to their beneficial properties, which can be achieved at a lower cost than silver and gold.[41] Like other noble metals, copper demonstrates thermal and electrical conductivity, making it suitable for use in electronic systems and conductive inks.[42] It also possesses antimicrobial properties and is readily available. These characteristics contribute to the appeal of Cu-NP synthesis as a research area. Various methods for synthesizing Cu-NPs exist, including thermal reduction, metal-vapor synthesis, chemical reduction, vacuum vapor deposition, radiation methods, microemulsion techniques, polyol processes, and laser ablation.[43] The synthesis of nanoparticles in polymer media is promising due to the ease of processing, solubility, lower toxicity, and the ability to control the growth of the resulting nanoparticles.[44]

Chitosan is chosen as a stabilizer for Cu-NPs because it can chelate metals, making it an excellent candidate for metal nanoparticle synthesis.[45] The use of biopolymers as stabilizing agents in the production of copper nanoparticles (Cu-NPs) is gaining popularity due to their abundance, compatibility with biological systems, and low toxicity

METHODOLOGY

The materials used for this research were inspected in order to avoid errors and contaminations. These materials are subdivided into two; laboratory apparatus and sample materials.

Sample Collection

Pure chitosan powder was bought from a commercial vendor and no further test or purification was conducted on it. The spider webs were collected from the roofs of building in the school premises.

Sample Pre-treatment

The spider web was washed with double distilled water to eliminate all unnecessary attachment on the spider web material and oven dried at 40°C for 24 hours to a constant weight.

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Sample Preparation

The pure chitosan powder underwent an acid hydrolysis to enable proper dissolution. The chitosan powder (0.9 g) was mixed in a solution of 1 % acetic acid (90 mL) and stirred for about 1 hour using a magnetic stirrer to enable complete dissolution.

The spider web powder (0.1 g) was dissolved in 15 % NaOH solution (100 mL) and stirred vigorously for 2 hours 30 minutes using a magnetic stirrer until it is properly dissolved then filtered into a separate flask using a Whatman filter paper (No. 1) and a funnel.

Bio-composites Blending

The chitosan solution (**18** mL) was shared in six different test tubes. The spider web solution (**3.6** mL) was added to each of the test tubes in an increasing proportion (increasing by **2** of **3.6** mL) and was labeled **5**:**1**, **5**:**2**, **5**:**3**, **5**:**4**, **5**:**5** and **5**:**6**. The ratio of **5:5** was prepared as a blank, this was done in other to obtain a more suitable composite blend which was characterized using the XRD analysis.

Copper Nanoparticle Synthesis

The synthesis process for copper nanoparticles involved three main steps; Preparation of aqueous $CuSO_4$ and ascorbic acid solution then reduction of Cu(II) ion by ascorbic acid to form copper nanoparticles and finally, separation and purification of copper nanoparticles, as adapted by Chandran et al.[46]

5.4 g of $CuSO_4$ was dissolved in **100** mL of distilled water and **0.78** g of ascorbic acid was also dissolved in **10** mL of distilled water. The both add the solutions were mixed together and stirred vigorously then allowed overnight in order to complete the reduction process. Finally, the solution was centrifuged using Fischer centrifuge (model **208**) with a rmp of **3400** for **15** minutes to separate the copper nanoparticles from the solution.

Copper nanoparticles (**0.3** g) was mixed with **1** M HCl (**10** mL) and stirred for **60** minutes. To further enhance the process of synthesizing copper nanoparticles, the solution was heated in a water bath at a temperature of **80-100**°C for **30-60** minutes to reduce the particle size and form a homogenous solution. After the heating process was completed, the solution was kept to cool at room temperature and filtered to remove any undissolved particles.

Composite Incorporated Copper Nanoparticle Formulation

The synthesized copper nanoparticles solution (**2** mL) was also added to the five chitosan-spider web mixture (leaving out the blank) and stirred vigorously in other to stabilize the synthesized copper nanoparticles using the biopolymer blends. The composite mixture was then casted onto an evaporating dish and placed in an incubator at **65** ^{0}C to obtain a dried composite blend which was then sent for further analysis.

Composite Analysis/ Characterization

The obtained copper nanoparticles incorporated composite blends were subjected to further analysis which involved various characterization methods to identify their specific properties. For optical properties, UV-vis spectrophotometer was used to record the absorption spectrum of the blank (chitosan-spider we blend (**5**:**5**)) and of all the five different samples. The functional groups were determined through the analysis of the FTIR spectrum. And the nature of the composite blends as well as the particle size of the incorporated Cu-NPs were characterized by using XRD analysis. The average crystalline size of the CuNPs was calculated using the Debye-Scherrer' equation as shown below;

Where K = Scherrer' constant (**0.9**)

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λ = Wavelength of CuKa (**1.54056** Å)

β = Full width at half maximum value (FWHM) in radian

ϴ = Half diffraction angle.

RESULTS AND DISCUSSION

The results obtained from the experimental procedures adapted for this study are all outlined and also discusses using related cases.

Result on UV-visible Analysis

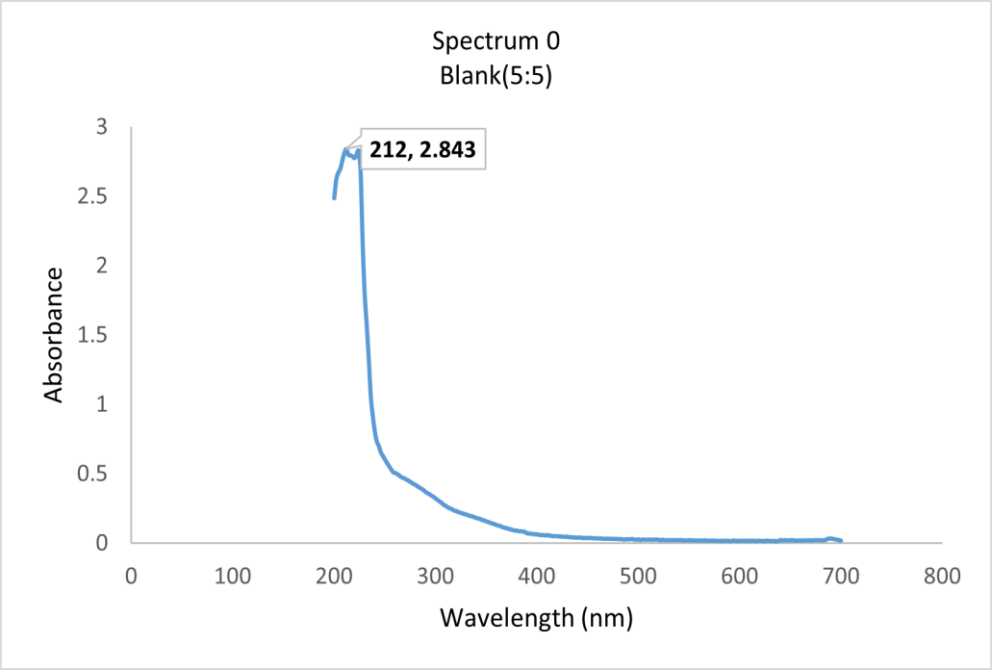

Figure 10 (a): UV-spectrum for the composite blend of chitosan-Spider web (as blank)

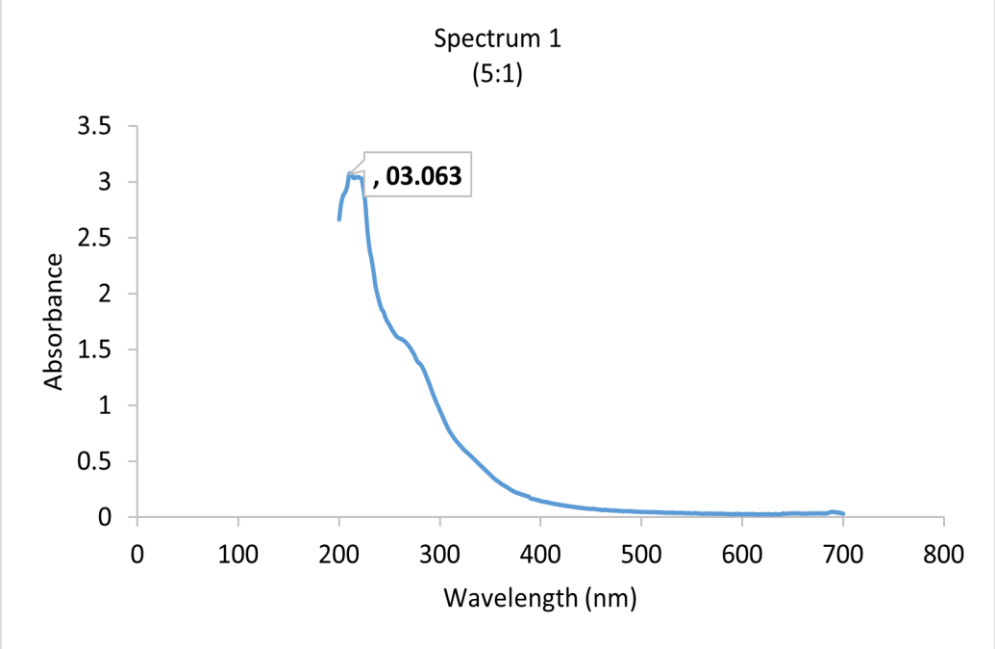

Figure 10 (b): UV-spectrum for the composite blend of chitosan-Spider web Cu-NPs (5:1)

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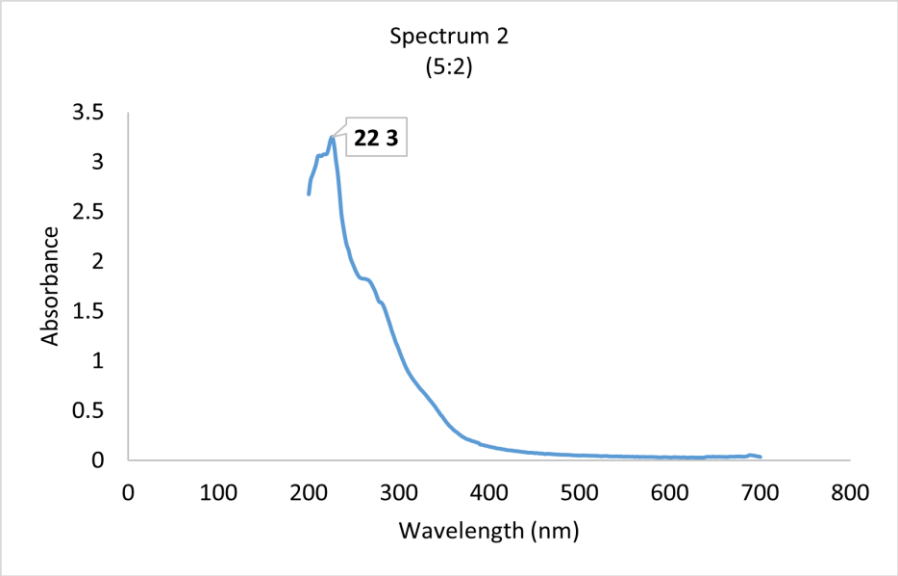

Figure 10 (c): UV-spectrum for the composite blend of chitosan-Spider web Cu-NPs (5:2)

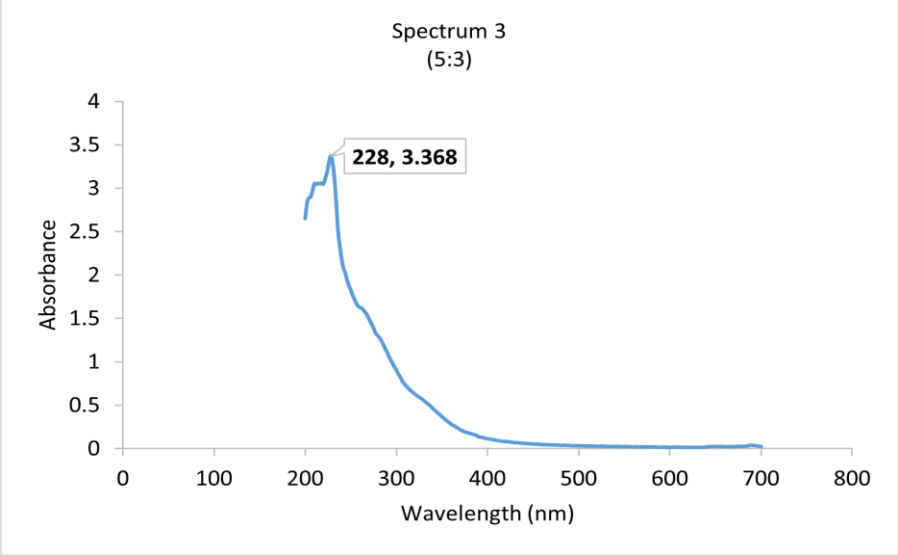

Figure 10 (d): UV-spectrum for the composite blend of chitosan-Spider web Cu-NPs (5:3)

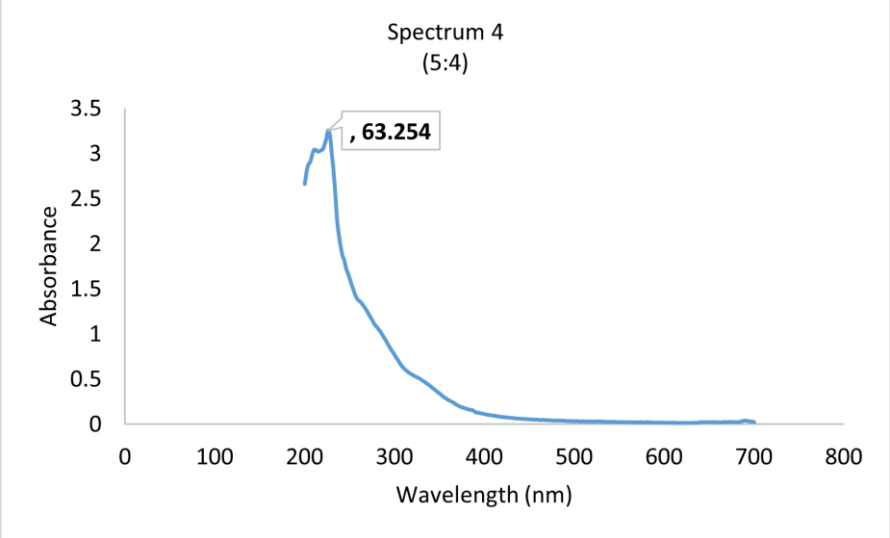

Figure 10 (e): UV-spectrum for the composite blend of chitosan-Spider web Cu-NPs (5:4)

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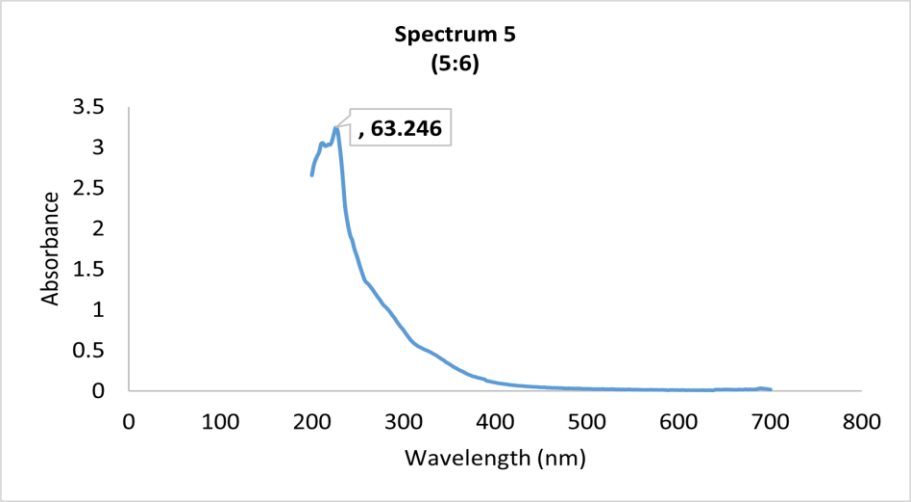

Figure 10 (f): UV-spectrum for the composite blend of chitosan-Spider web Cu-NPs (5:5)

The five samples were scanned at the wavelength range of **200-700** nm (with the blank inclusively) using the UV model **7415** Jenway UV-visible spectroscopy. All samples showed peaks within the range of **212-228** nm (as shown in figure **10** (a)-(f) above). The blank (spectrum **0**) showed its maximum absorbance of **2.843** at **212** nm, Spectrum **1** showed its maximum absorbance of **3.071** at the wavelength of **212** nm, spectrum **2** showed its maximum absorbance of **3.251** at the wavelength of **226** nm, spectrum **3** showed its maximum absorbance of **3.36** at the wavelength of **228** nm, spectrum **4** showed its maximum absorbance of **3.254** at the wavelength of **226** nm and spectrum **5** showed its maximum absorbance of **3.246** at the wavelength of **226** nm. There was a shift in the absorption peak of the five samples (Cu-NPs incorporated chitosan-spider web blends) as compared to the blank (which is a pure blend of chitosan-spider web solution). The findings obtained from the UV-visible spectroscopic analysis confirmed the presence of copper nanoparticles in the synthesized composite blends as it has been reported in the literature that the absorption peak in the range of **200**–**300** nm is a characteristic feature of CuNPs.[47,48]

Result on the FTIR Analysis

Table 3.1.1 FTIR Analysis of Pure Ccob

Absorption (cm^{-1})	**Functional groups**	**Appearance**
3459.0	N-H stretching	Medium
3049.0	O-H stretching	Weak broad
2105.9	CΞC stretching	Weak
1677.3	C=O stretching	Medium
1561.8	N-H bending	Medium
1442.5	C-H bending	Strong

Table 3.1.2 FTIR Analysis of Ccob-NPs

Absorption (cm^{-1})	**Functional groups**	**Appearance**
3365.8	N-H and O-H stretch interference	Strong
2124.6	N=C=O stretching	Weak
2467.5	C-M	Weak
1636.3-1561.8	N-H bending	Medium
1431.3-1394	C-H bending	Strong

C-M = Chitosan-Metal bond

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The FTIR analysis was carried out to determine the molecular interaction between the chitosan-spider web (Ccob) biocomposite blend and the synthesized Cu-NPs. The FTIR spectrum of the pure chitosan-spider web (Ccob) and composite incorporated copper nanoparticles (Ccob-CuNPs) as shown in Table **4.2** and **4.2.1** respectively, shows a band at **3459.0** cm^{-1} and **3365.8** cm^{-1} which corresponds to N-H interference of O-H stretch. It also shows a transmission band at **2124.6** cm^{-1} which is assigned to N=C=O stretching. The band at **1636.3** and **1561.8** cm^{-1}corresponds to the N-H bending of an amine and the band at **1431.3** and **1394** cm^{-1} corresponds to the C-H bending of an alkane. The FTIR spectrum of the Ccob-CuNPs also showed the formation of new vibration band at **2467.5** cm^{-1} corresponding to the C-M bond, implying the capping of the nanoparticles by the biocomposite. These results correspond to the findings of Dang et al.[49]

Result on XRD Analysis

Table 3.1.3 Peak List Obtained from XRD Analysis of Ccob-NPs

2θ (°)	FWHM	d-spacing (Å)	Rel. Int. (%)	Hkl
17.1342	**0.9446**	**5.17519**	**3.88**	**010**
32.8272	**0.3936**	**2.72831**	**16.57**	**011**
34.1350	**0.1181**	**2.62672**	**21.64**	**100**
36.5464	**0.2362**	**2.45875**	**13.65**	**101**
37.9921	**0.1378**	**2.36845**	**100.00**	**111**
44.2114	**0.1574**	**2.04864**	**16.85**	**200**
45.4435	**0.4723**	**1.99592**	**7.64**	**201**

FWHM = Full Width at Half Maximum (β), Hkl = Miller's indices

The crystallinity of the CuNPs was examined by powder X-ray diffraction (XRD) analysis and the XRD profile (as shown in table **4.3**) was obtained. The diffraction of Cu NPs exhibited several peaks of 2Θ = **17.1342^0**, **32.8272^0**, **34.1350^0**, **36.5464^0**, **37.9921^0**, **44.2114^0** and **45.4435^0** which are in correlation with the diffraction planes. From the spectra, seven peaks were observed with the miller indices (hkl) planes of (**010**), (**011**), (**100**), (**101**), (**111**), (**200**) and (**201**) which are attributed to the face centered cubic (fcc) phase and were consistent to the standard data for Cu (JCPDS No. **04**–**0836**). The average crystalline size (T_{xrd}) was calculated using Debye-Scherrer's equation. From the highest miller index (**111**) diffraction plane, the average crystalline size was found to be around **57.8** nm. The obtained XRD results clearly confirmed the formation of CuNPs synthesized using a biopolymer medium as it is in line with the findings of Usman et al.[50]

CONCLUSION

In conclusion, the results obtained from this research confirms successful synthesis and characterization of chitosan-spider web biopolymer blends, as well as incorporated copper nanoparticles. The UV-vis results of the samples, as compared to the blank, showed a significant shift in the absorption of light at specific wavelength, which indicated the formation of the nanoparticles. The FTIR results showed the formation of new vibration band at **2467.5** cm^{-1} corresponding to the C-M bond, implying the capping of the nanoparticles by the biocomposite as compared to the findings of literature. The result obtained from the XRD analysis confirmed the synthesis of CuNPs. The average size of the CuNPs was also estimated to be **57.8** nm using the Debye-Scherrer' formula. These findings have opened up new avenues for the development of advanced materials with enhanced properties and diverse applications. This research has demonstrated the successful combination of biopolymers and metallic nanoparticles, leading to materials with improved functionalities and potential applications in various fields. The successful blending of chitosan and spider web biopolymer has been confirmed through advanced analytical techniques such as UV-visible spectroscopy, Fourier-transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD), which have provided insights into their morphology, crystalline structure, and chemical interactions.

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The potential applications of chitosan and spider web biopolymer blends, as well as copper nanoparticles, are vast and promising. In the biomedical field, these materials have demonstrated biocompatibility, antimicrobial properties, and controlled drug release capabilities, making them suitable for wound healing dressings, tissue engineering scaffolds, and drug delivery systems.[51] Furthermore, these materials have potential applications in environmental remediation, water treatment, and packaging, benefiting from their adsorption properties, biodegradability, and mechanical strength.[52]

However, further research is necessary to optimize the synthesis processes, improve the stability and scalability of the materials, and thoroughly evaluate their long-term stability, toxicity, and biocompatibility as exploring the potential synergistic effects between the chitosan and spider web biopolymer blends and copper nanoparticles could lead to the development of advanced multifunctional materials with enhanced properties and expanded applications.

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