

Article

Chitosan-Stabilized Silver Nanoparticles for Antimicrobial Polyester Finishing by Exhaustion Dyeing: A Critical Assessment of Synthesis-to-Textile Transferability

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Abstract

Chitosan-stabilized silver nanoparticles are promising antimicrobial agents for textile finishing, but their direct transfer from colloidal synthesis to polyester fabrics is limited by nanoparticle deposition, dispersion stability, and fiber–particle interactions. This study evaluated three reported chitosan-assisted silver nanoparticle routes for antimicrobial polyester finishing by exhaustion dyeing. The Ag-containing systems were characterized by UV-Vis spectroscopy, dynamic light scattering, thermogravimetric analysis, X-ray diffraction, scanning electron microscopy coupled with energy-dispersive spectroscopy, atomic absorption spectroscopy, and qualitative antimicrobial assays. The NaBH₄-assisted route showed the most defined plasmonic band, with λ_{max} at 408 nm before freeze-drying and 400 nm after redispersion. DLS indicated large apparent hydrodynamic diameters before freeze-drying, which shifted from 439.8, 357.2, and 653.5 nm to 28.7, 29.8, and 38.1 nm after drying/freeze-drying and redispersion for M1, M2, and M3, respectively. XRD confirmed metallic silver mainly in M1 and M2, while SEM/EDS revealed low silver incorporation on polyester fabrics, with 0.69, 0.11, and 0.20 at.% Ag. PET-M3 showed the clearest antimicrobial inhibition and the highest operationally extracted silver. These results indicate that effective antimicrobial polyester finishing requires improved purification, dispersion control, quantitative antimicrobial validation, and nanoparticle–fiber anchoring.

Keywords: silver nanoparticles; chitosan; polyester fabric; antimicrobial finishing; exhaustion dyeing; textile functionalization



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1. Introduction

Polyester is one of the most widely used synthetic fibers in the textile industry because of its low cost, mechanical resistance, dimensional stability, durability, and compatibility with large-scale dyeing and finishing processes [1]. Beyond conventional clothing applications, polyester fabrics have increasingly been investigated as platforms for functional textiles, including materials with antimicrobial, self-cleaning, ultraviolet-protective, flame-retardant, and sensing properties [2,3]. Among these functionalities, antimicrobial finishing is particularly relevant for healthcare textiles, sportswear, protective clothing, and other

applications in which microbial contamination, odor formation, and biofilm development can reduce material performance and user safety [4,5].

Silver nanoparticles (AgNPs) are among the most studied antimicrobial nanomaterials due to their broad-spectrum activity against Gram-positive and Gram-negative bacteria, which is commonly associated with the release of Ag⁺ ions, membrane disruption, oxidative stress, and interactions with intracellular biomolecules [6–8]. However, the antimicrobial activity of AgNPs depends strongly on their size, morphology, surface chemistry, aggregation state, and ability to release silver species under use conditions [6,9,10]. Therefore, the synthesis route and the stabilizing agent play a central role in determining both colloidal properties and biological response. Chitosan, a cationic biopolymer derived from chitin, has been widely employed as a stabilizing, coating, or reducing agent in metal nanoparticle synthesis because of its amino and hydroxyl groups, film-forming ability, biocompatibility, and intrinsic antimicrobial activity [11,12]. These same properties, however, may complicate the interpretation of antimicrobial results, since bacterial inhibition in AgNP/chitosan systems can arise from silver, chitosan, residual reagents, or synergistic effects among these components [11–13].

Several studies have reported chitosan-assisted routes for preparing AgNPs with promising optical, structural, and antimicrobial properties [14–16]. In many cases, the successful formation of AgNPs is confirmed by the appearance of a surface plasmon resonance band in the visible region, together with microscopic or diffraction evidence of metallic silver [10,14–16].

The three routes selected in the present study were chosen because they represent distinct chitosan-assisted strategies for obtaining Ag-containing systems, rather than variations of the same synthetic approach. The first route is based on fast chemical reduction with NaBH₄ in the presence of chitosan, favoring rapid Ag⁰ formation under strong reducing conditions [14]. The NaBH₄-assisted route was included as a strong-reduction reference because it promotes rapid Ag⁺ reduction in the presence of chitosan, whereas replacing NaBH₄ with a milder reducing agent, such as ascorbic acid, would change the reaction kinetics, pH conditions, surface chemistry, and Ag/chitosan interactions, thus constituting a different synthetic route requiring independent optimization. The second route involves a two-step alkaline process, in which chitosan first interacts with AgNO₃ and is then exposed to concentrated NaOH, producing structured Ag-containing chitosan materials [15]. The third route is a one-pot alkaline/thermal process, without NaBH₄, in which silver reduction occurs under milder alkaline conditions and prolonged heating [16]. Thus, these three routes were selected to cover contrasting reducing environments, pH conditions, reaction times, thermal exposure, physical states of the product, and expected dispersion behaviors. This comparison was considered sufficient to evaluate synthesis-to-textile transferability across representative Ag/chitosan systems without turning the study into a broad optimization of all possible synthetic routes.

Nevertheless, the direct translation of these colloidal syntheses into textile finishing is not straightforward. Polyester has a hydrophobic and chemically inert surface, and the lack of reactive functional groups limits the spontaneous adhesion of hydrophilic polymers and inorganic nanoparticles without previous surface activation, binders, crosslinkers, plasma treatment, or other anchoring strategies [17,18]. As a result, nanoparticle formation in solution does not necessarily guarantee efficient deposition, homogeneous distribution, durability, or antimicrobial performance when the same material is applied to polyester fibers.

Conventional antimicrobial finishing methods, such as padding, coating, impregnation, plasma-assisted deposition, and in situ reduction on fibers, have been used to incorporate silver-based materials onto textile substrates [5,17–19]. These approaches can

improve functionality but may require additional processing steps, chemical binders, surface activation, or post-treatment washing to remove unfixed species [17–19]. Exhaustion dyeing, by contrast, is already established in the textile industry and could represent a practical route for incorporating functional nanomaterials during a conventional wet-processing step. However, for polyester fabrics, this strategy requires the nanomaterial to withstand high-temperature dyeing conditions while maintaining sufficient affinity for the fiber surface. The limited number of studies addressing this synthesis-to-textile transferability highlights the need for a critical evaluation of whether AgNP/chitosan systems reported in the literature can be directly used for antimicrobial polyester finishing.

In this work, these three-representative chitosan-assisted silver nanoparticle synthesis routes were reproduced or adapted and applied to polyester fabrics by exhaustion dyeing. The resulting Ag-containing systems were evaluated before and after freeze-drying/redispersion using UV-Vis spectroscopy, dynamic light scattering, thermogravimetric analysis, X-ray diffraction, scanning electron microscopy coupled with energy-dispersive spectroscopy, atomic absorption spectroscopy, and qualitative antimicrobial assays. Rather than presenting an optimized antimicrobial textile, this study critically assesses the relationship between nanoparticle formation, dispersion behavior, silver deposition on polyester, operational silver extraction, and antimicrobial response. The results show that the formation of Ag-containing chitosan systems does not necessarily ensure effective antimicrobial finishing of polyester, mainly because of low silver incorporation into the fabric and possible contributions from chitosan or residual alkaline species.

2. Materials and Methods

2.1. Materials

Silver nitrate AgNO_3 (Sigma Aldrich/BioXtra—São Paulo/Brazil), acetic acid (VETEC—Rio de Janeiro/Brazil), sodium borohydride NaBH_4 (VETEC—Rio de Janeiro), sodium hydroxide NaOH (Ciavikko—Sabará/Brazil), sodium chloride NaCl (NEON—Suzano/Brazil), nitric acid HNO_3 (NEON—Suzano/Brazil), and deionized water were used for the synthesis, redispersion, textile functionalization, and operational silver extraction assays. A commercial white 100% polyester plain-weave fabric was used as the textile substrate and was provided by Parantex (Apucarana, PR, Brazil). The fabric had a mass per unit area of $160 \pm 5 \text{ g m}^{-2}$, determined according to ABNT NBR 10591, with 20 tex warp yarn and 6.25 tex weft yarn. The fabric density was 24 yarns cm^{-1} in both warp and weft directions. The fabric was used without previous chemical surface treatment. Microbiological assays were performed using *Staphylococcus aureus* ATCC 25923, and *Klebsiella pneumoniae* ATCC 13883. Mueller–Hinton agar, MacConkey agar, mannitol salt agar, tryptic soy broth, and sterile phosphate buffer (KASVI—Pinhais/Brazil) were used for microbial cultivation and antimicrobial screening. All reagents were used as received, without further purification. Chitosan used in the experiments was acquired from Chem-Gold (São Paulo/Brazil) and had a purity higher than 80%, a degree of deacetylation higher than 75%, and a viscosity-average molecular weight in the range of 50,000–190,000 Da, according to the supplier. Based on this molecular weight range and the nominal degree of deacetylation, the estimated degree of polymerisation was approximately 290–1180.

2.2. Synthesis of Ag-Containing Chitosan Systems

Three chitosan-assisted routes were reproduced or adapted from previously reported procedures and coded as M1, M2, and M3. The products were evaluated as Ag-containing chitosan systems because silver nanoparticles, chitosan, and residual synthesis components may coexist in the final materials.

For M1, a chitosan/ NaBH_4 -assisted route was carried out according to Ahmad et al. [14], with minor operational adjustments. NaBH_4 was used to reproduce this reported strong-reduction route and to provide a reference system for comparison with the NaOH-assisted routes, rather than as a sustainability-oriented reducing agent. A 2.0% (*w/v*) chitosan solution was prepared by dissolving chitosan in 50 mL of 1% acetic acid solution. Then, 50 mL of 0.01 M AgNO_3 solution was added, and the mixture was kept under magnetic stirring for 2 h at room temperature. After this period, 20 mL of 0.04 M NaBH_4 solution was added to the reaction medium. The color immediately changed from pale yellow to brown, indicating silver reduction. The suspension was kept under magnetic stirring for an additional 1 h. The final M1 product was obtained as a colloidal suspension and used for UV-Vis, DLS, antimicrobial screening, textile functionalization, and freeze-drying.

For M2, a two-step chitosan/NaOH route was adapted from Mirda et al. [15]. First, a 2.0% (*w/v*) chitosan solution was prepared in 1% acetic acid under magnetic stirring for 3 h, or until complete dissolution. Then, 10 mL of 0.118 M AgNO_3 solution was slowly added under continuous stirring, and the mixture was maintained under agitation for 24 h. The resulting gel-like material was carefully dropped into 25 mL of 12.5 M NaOH solution using a dropper, replacing the syringe pump used in the original procedure. After approximately 15 min, the system changed to a brown color, suggesting silver reduction and the formation of Ag-containing chitosan spheres. The material was centrifuged at 6000 rpm for 10 min, the supernatant was discarded, and the solid fraction was washed twice with 30 mL of deionized water to remove excess alkaline residues. Finally, the material was dried in an oven at 40 °C for 1 h. The obtained solid material was used for characterization, antimicrobial screening, redispersion, and textile functionalization.

For M3, a one-pot chitosan/NaOH route was adapted from Kalaivani et al. [16]. A 0.2% (*w/v*) chitosan solution was prepared in 1% acetic acid under magnetic stirring for 30 min. Subsequently, 3.0 mL of 0.1 M AgNO_3 solution was added, followed by 100 μL of 1 M NaOH solution. The reaction mixture was kept under magnetic stirring at 90 °C for 10 h using an oil bath. During the reaction, the solution changed from colorless to pale yellow and then to brown-yellow, indicating silver reduction. The final M3 product was obtained as a colloidal suspension and used for UV-Vis, DLS, antimicrobial screening, textile functionalization, and freeze-drying.

2.3. Freeze-Drying and Redispersion

The products obtained from M1, M2, and M3 were converted into solid Ag-containing chitosan materials for additional characterization and antimicrobial screening. For M1 and M3, defined volumes of the final suspensions were frozen in beakers protected with aluminum foil and freeze-dried using a freeze-dryer (SL-404, SOLAB, Sao Carlos, Brazil). The freeze-drying time varied from 2 to 5 days, depending on the sample volume and drying behavior. After complete drying, the materials were stored protected from light until use.

For M2, the synthesis produced a gel-like material that was dropped into concentrated NaOH, centrifuged, washed, and dried as described in Section 2.2. Therefore, although M2 was also redispersed in deionized water using the same nominal initial volume of the experiment, its redispersed form should be interpreted with additional caution because centrifugation, washing, and drying may have removed soluble species and modified the composition of the recovered solid material.

For redispersion, the dried materials obtained from M1, M2, and M3 were reconstituted in deionized water using the same nominal initial volume of each respective experiment and sonicated until visual homogenization. Thus, the redispersed samples were prepared under

nominally volume-equivalent conditions relative to their initial preparations. Nevertheless, UV-Vis and DLS results after redispersion were interpreted with caution, since drying, freeze-drying, washing, and sonication can modify the aggregation state, hydrodynamic population, composition, and interactions between silver-containing domains and the chitosan matrix.

2.4. Polyester Functionalization by Exhaustion Dyeing

Polyester fabrics were functionalized with the Ag-containing chitosan systems using an exhaustion dyeing procedure in a laboratory dyeing machine (Kimak AT1-SW, Brusque, Brazil). For each treatment, 15 mL of Ag-containing suspension or redispersed freeze-dried material was diluted with 45 mL of deionized water, giving a final bath volume of 60 mL. The liquor ratio was 40 mL g⁻¹, and 1.5 g of polyester fabric was used for each dyeing experiment. The fabric samples were individually placed in dyeing vessels containing the respective Ag-containing chitosan system and processed for 45 min at 130 °C. After dyeing, the fabrics were removed from the bath and dried at room temperature. The treated fabrics were coded according to the system used for functionalization: PET-M1, PET-M2, and PET-M3.

2.5. Physicochemical Characterization

UV-Vis spectroscopy was performed using a Cary 60 UV-Vis spectrophotometer (Agilent Technologies, Santa Clara, CA, USA). The spectra were recorded from 200 to 800 nm using quartz cuvettes with a 10 mm optical path. Approximately 4.0 mL of each liquid sample was used for the measurements. For freeze-dried samples, the materials were redispersed in deionized water under sonication prior to analysis.

Dynamic light scattering (DLS) measurements were performed using a Litesizer 500 particle size analyzer (Anton Paar, Graz, Austria). Approximately 4.0 mL of each dispersion was transferred to disposable acrylic cuvettes. The measurements were conducted at 25 °C using automatic angle selection, automatic focus and filter settings, and the general-purpose analysis model. Water was used as the dispersing medium. The refractive index and absorption index for silver were set to 0.159 and 4.3, respectively. The reported values correspond to the main hydrodynamic diameter distribution peaks and were used to compare dispersion behavior before and after freeze-drying/redispersion.

Thermogravimetric analysis (TGA) was performed using a TGA-50 analyzer (Shimadzu, Kyoto, Japan). Approximately 6 mg of each freeze-dried sample was heated from 25 to 800 °C under argon atmosphere at a heating rate of 10 °C min⁻¹. Argon was selected to evaluate the thermal degradation behavior of the Ag-containing chitosan systems under inert conditions and to minimize oxidative combustion of the organic matrix, allowing comparison of the intrinsic thermal behavior of the three materials.

Scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM/EDS) was used to evaluate the morphology and elemental composition of the freeze-dried Ag-containing chitosan systems and the treated polyester fabrics. The analyses were performed using a TESCAN VEGA microscope (TESCAN, Brno, Czech Republic). Freeze-dried samples were dispersed onto carbon tape and dried before analysis. Polyester fabric samples were directly fixed onto carbon tape. All samples were gold-coated prior to SEM imaging to improve electrical conductivity. EDS mapping was used mainly to identify the distribution of silver, carbon, oxygen, nitrogen, and sodium. The EDS results were treated as local semi-quantitative data.

X-ray diffraction (XRD) was performed using a D2 Phaser diffractometer (Bruker, Karlsruhe, Germany) equipped with CuK α radiation (λ = 1.54 Å; 8.047 keV). Freeze-dried samples were analyzed as powders, whereas polyester fabrics were analyzed directly. The

diffraction patterns were collected from 2° to 60° in 2θ , with an angular increment of 0.033° and a scan rate of $2^{\circ} \text{ min}^{-1}$.

2.6. Operational Silver Extraction from Functionalized Fabrics

The amount of extractable silver from the functionalized polyester fabrics was evaluated by atomic absorption spectroscopy using an operational saline extraction procedure. Each treated fabric sample was immersed in 0.9% NaCl solution and kept under agitation at 37°C and 100 rpm for 1 h. After contact with the textile sample, the liquid phase was collected and acidified with 0.5 mL of HNO_3 prior to analysis. Silver quantification was performed using an ICE 3000 atomic absorption spectrophotometer (Thermo Scientific, Waltham, MA, USA). Calibration was carried out using aqueous silver standards from 1 to 5 mg L^{-1} . The results were expressed as the concentration of silver extracted into the saline medium under the tested conditions.

2.7. Antimicrobial Screening of Ag-Containing Systems and Functionalized Fabrics

The antimicrobial activity of the Ag-containing chitosan systems was evaluated by a qualitative disk diffusion assay. For liquid samples, 15 μL of each suspension was impregnated onto sterile paper disks with 6 mm diameter. For freeze-dried samples, a small portion of each dried material was directly deposited onto the paper disks. The disks were placed onto agar plates previously inoculated with 100 μL of bacterial suspension containing approximately 10^6 CFU mL^{-1} . The assays were performed against *S. aureus* ATCC 25923 and *K. pneumoniae* ATCC 13883. The plates were incubated at 37°C for 24 h, and antimicrobial activity was evaluated visually based on the presence or absence of inhibition zones. When visible, inhibition halos were measured approximately and reported as qualitative indicators of antimicrobial response.

The antimicrobial response of functionalized polyester fabrics was evaluated using an adapted ASTM E2149-13 procedure. Fresh bacterial cultures were prepared in sterile tryptic soy broth at $35 \pm 2^{\circ}\text{C}$ for 24 h and then diluted in sterile 0.3 mM monopotassium phosphate buffer to approximately $1.5\text{--}3.0 \times 10^5 \text{ CFU mL}^{-1}$, corresponding to approximately 0.5 McFarland. Fabric samples of 20 mm $\times$ 20 mm were sterilized by UV exposure and placed in contact with 50 mL of bacterial suspension under agitation at 110 rpm for 1 h. After contact, serial dilutions were prepared and plated in duplicate using MacConkey agar for *K. pneumoniae* ATCC 13883 and mannitol salt agar for *S. aureus* ATCC 25923. A bacterial suspension without fabric was used as positive control. The assay was interpreted qualitatively, based on visual comparison of bacterial growth between control and treated samples. Therefore, the textile antimicrobial assay should be considered a screening test rather than a standardized quantitative determination of antimicrobial efficiency.

2.8. Data Availability, Ethical Statement, and Use of Generative AI

The data supporting the findings of this study are available from the corresponding author upon reasonable request. No large public datasets or computer codes were generated or analyzed in this study. This work did not involve human participants, human biological material, or animals; therefore, ethical approval was not required. Standard laboratory biosafety procedures were followed for handling ATCC bacterial strains.

Generative artificial intelligence tools (Grammarly, GPT-5.5 Thinking) were used to assist with manuscript organization, language refinement, and formatting of selected sections. All scientific content, experimental descriptions, data interpretation, and conclusions were checked and approved by the authors.

3. Results

3.1. Visual Appearance of Ag-Containing Chitosan Systems and Treated Polyester Fabrics

The three chitosan-assisted synthesis routes produced Ag-containing systems with distinct visual characteristics. In M1, the addition of NaBH_4 to the chitosan/ AgNO_3 mixture caused an immediate color change from pale yellow to brown, indicating silver reduction. In M2, the chitosan/ AgNO_3 mixture formed a gel-like material after 24 h of stirring, and brown Ag-containing chitosan structures were obtained after the material was dropped into concentrated NaOH . In M3, the initially colorless chitosan/ AgNO_3 mixture gradually changed to pale yellow and then to brown-yellow during the 10 h reaction at 90°C . Representative images of the final products obtained from the three routes are shown in Figure S1.

After exhaustion dyeing, the originally white polyester fabrics acquired different color intensities depending on the Ag-containing system used. Representative images of the treated fabrics are shown in Figure S2.

3.2. UV-Vis Spectroscopy of Ag-Containing Chitosan Systems

UV-Vis spectroscopy was used to evaluate the optical response of the Ag-containing chitosan systems before and after freeze-drying/redispersion. The spectra are shown in Figure 1, and the main optical parameters are summarized in Table 1. In these systems, the position, intensity, and width of the visible absorption band provide complementary information about the silver-containing domains and their interaction with the chitosan matrix. The λ_{max} value is associated with the localized surface plasmon resonance of metallic silver domains and may shift depending on particle size, aggregation state, surface chemistry, and the dielectric environment provided by the chitosan matrix. The maximum absorbance reflects the intensity of the optical response, but it should not be interpreted as a direct quantitative measurement of AgNP concentration because it can also be affected by scattering, matrix absorption, aggregation, and redispersion efficiency. The full width at half maximum (FWHM) provides an indication of the breadth of the plasmonic response; narrower bands generally suggest a more defined optical population, whereas broader bands indicate greater heterogeneity, aggregation, or overlapping contributions from different silver-containing species and the chitosan matrix.

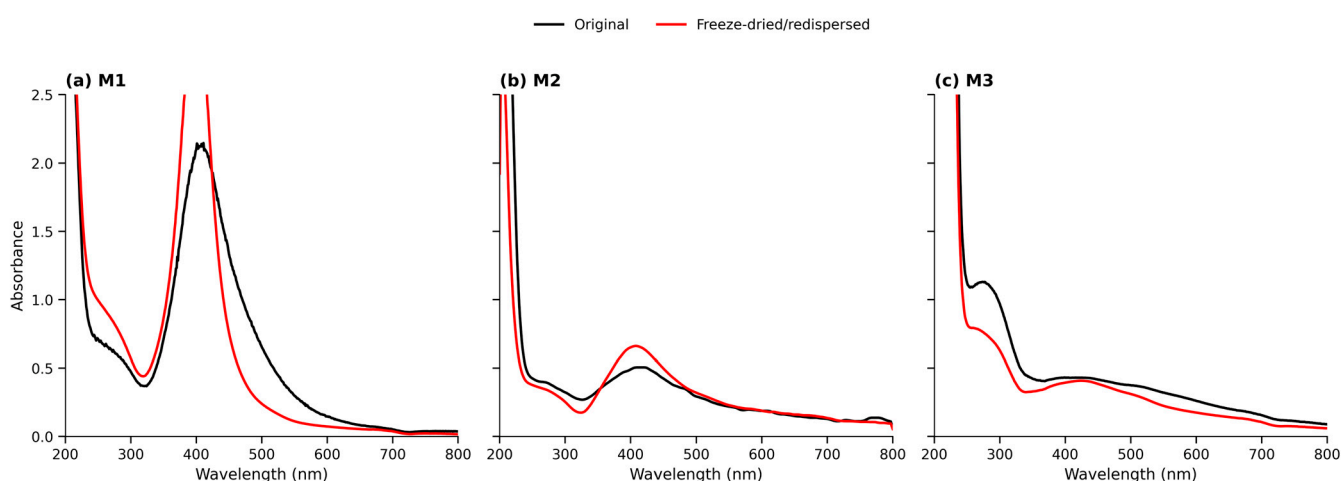


Figure 1. UV-Vis spectra of Ag-containing chitosan systems before and after drying/freezing and redispersion. (a) M1, (b) M2, and (c) M3. Black lines correspond to the original suspension or product obtained after synthesis, and red lines correspond to the dried material redispersed in deionized water using the same nominal initial volume of each respective experiment.

Table 1. Optical parameters obtained from UV-Vis spectra of Ag-containing chitosan systems before and after freeze-drying/redispersion.

Sample	Condition	λ_{max} (nm)	Absmax	FWHM (nm)
M1	Original suspension	408	2.1	89
M1	Freeze-dried/redispersed	400	3.1	63
M2	Original product	420	0.6	143
M2	Freeze-dried/redispersed	407	0.7	127
M3	Original suspension	420	0.3	~170 *
M3	Freeze-dried/redispersed	425	0.4	~120 *

* Estimated after approximate baseline correction because the M3 spectra showed broad, low-intensity bands partially overlapped with the absorption contribution of the chitosan matrix.

M1 showed the most intense and defined absorption band in the visible region, with λ_{max} at 408 nm before freeze-drying and 400 nm after redispersion. The position of this band is consistent with the plasmonic response expected for silver-containing domains in a polymeric matrix. The slight blue shift after redispersion, together with the decrease in FWHM from 89 to 63 nm, suggests that freeze-drying followed by sonication/redispersion changed the dominant optical population, possibly by reducing the contribution of larger aggregates or improving the optical accessibility of smaller Ag-containing domains. The increase in maximum absorbance from 2.1 to 3.1 should therefore be interpreted as a change in optical response and dispersion state, rather than as direct evidence of increased silver concentration.

M2 exhibited a less intense and broader band, with λ_{max} values of 420 nm before freeze-drying and 407 nm after redispersion. Compared with M1, the lower Absmax and larger FWHM indicate a less defined plasmonic response, consistent with a more heterogeneous Ag-containing chitosan material. The decrease in FWHM from 143 to 127 nm and the blue shift after redispersion suggest partial modification of the dispersed population, although the band remained broader than that of M1.

M3 presented the weakest and least resolved optical response among the three systems, with λ_{max} at 420 nm before freeze-drying and 425 nm after redispersion. After approximate baseline correction, FWHM values of approximately 170 and 120 nm were estimated for the original and redispersed M3 samples, respectively. The low Absmax values and broad bands indicate a weak and heterogeneous optical response, probably due to lower definition of plasmonic silver domains, aggregation, and partial overlap with the absorption contribution of the chitosan matrix. Therefore, the UV-Vis results indicate that M1 produced the most optically defined Ag-containing system, M2 showed an intermediate and broader response, and M3 produced the least defined optical response.

3.3. DLS Analysis Before and After Freeze-Drying/Redispersion

DLS measurements were performed to compare the apparent hydrodynamic populations of the Ag-containing chitosan systems before and after freeze-drying/redispersion. The main hydrodynamic diameter peaks are summarized in Table 2. Number-weighted size distribution profiles are provided in Figure S3 as Supplementary Information.

Table 2. Main hydrodynamic diameter peaks obtained by DLS before and after freeze-drying/redispersion.

Sample	Before Drying/Freeze-Drying (nm)	After Drying/Freeze-Drying and Redispersion (nm)
M1	439.8	28.7
M2	357.2	29.8
M3	653.5	38.1

Before freeze-drying, all systems showed main hydrodynamic diameter peaks in the submicrometric range. M1, M2, and M3 presented main peaks at 439.8, 357.2, and 653.5 nm, respectively. After drying/freeze-drying and redispersion in deionized water using the same nominal initial volume of each respective experiment, the main peaks shifted to lower values: 28.7 nm for M1, 29.8 nm for M2, and 38.1 nm for M3. These values should be interpreted as comparative hydrodynamic indicators of the dominant detected populations rather than as direct measurements of the metallic silver core size, since DLS is affected by the chitosan matrix, solvation layer, aggregation state, and scattering contribution of larger particles.

3.4. Thermal Behavior of Freeze-Dried Ag-Containing Chitosan Systems

The thermal behavior of the freeze-dried materials was evaluated by TGA under argon atmosphere. The thermogravimetric curves are shown in Figure S4. M1 showed an initial mass loss event below approximately 150 °C, followed by a second mass loss event near 300 °C. M2 did not show a pronounced initial mass loss below 150 °C and exhibited a marked mass decrease starting near 200 °C. M3 showed an initial mass loss below approximately 100–150 °C, followed by another mass loss event between approximately 130 and 350 °C.

Although some mass loss associated with adsorbed water or volatile components occurred below or near the polyester dyeing temperature, the main thermal degradation events of the chitosan-containing matrices were observed above the temperature used in the exhaustion dyeing process. Because the measurements were performed under argon, the results should be interpreted as the thermal behavior of the materials under inert atmosphere. Oxidative degradation under air may occur differently and should be considered in future studies if thermo-oxidative stability during processing or use is specifically investigated.

3.5. X-Ray Diffraction of Freeze-Dried Ag-Containing Chitosan Systems

XRD patterns of the freeze-dried Ag-containing chitosan systems are shown in Figure 2. M1 displayed diffraction peaks assigned to metallic silver with a face-centered cubic structure, including reflections attributed to the (111), (200), (220), and (311) planes. Additional signals at lower 2θ values were also observed and were associated with the chitosan-containing matrix.

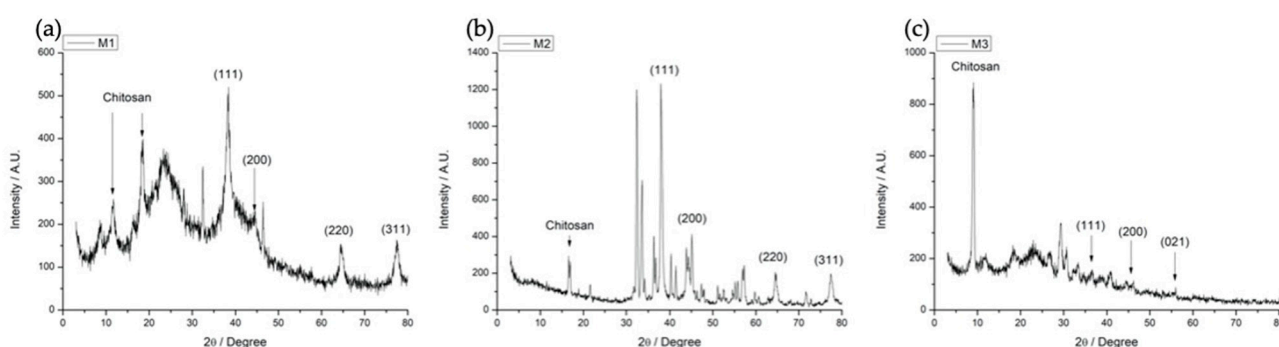


Figure 2. XRD patterns of freeze-dried Ag-containing chitosan systems. (a) M1, (b) M2, and (c) M3. The marked reflections correspond to the main diffraction planes of metallic silver with face-centered cubic structure.

M2 also showed diffraction peaks attributed to metallic silver, with reflections corresponding to the (111), (200), and (220) planes. In contrast, M3 showed less defined silver reflections. In this sample, the low-angle region showed contributions associated with the

chitosan matrix, and the reflections typically assigned to metallic silver were weaker than those observed for M1 and M2.

3.6. SEM/EDS Analysis of Freeze-Dried Ag-Containing Chitosan Systems

The morphology and elemental distribution of the freeze-dried Ag-containing chitosan systems were evaluated by SEM/EDS. Representative SEM images and Ag elemental maps are shown in Figure 3, and the semi-quantitative EDS data are summarized in Table 3. The full EDS spectra corresponding to the analyzed regions of the freeze-dried M1, M2, and M3 samples are provided in Figure S7.

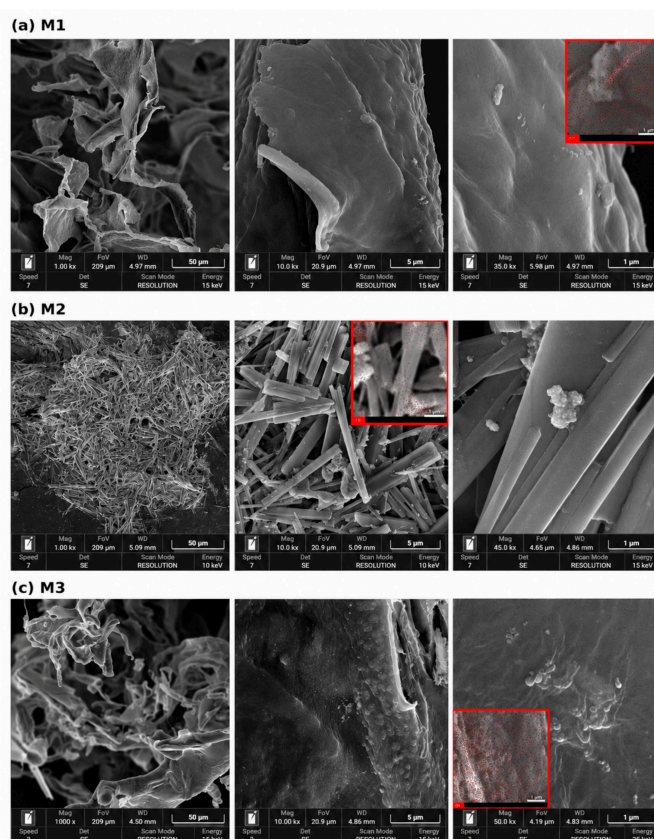


Figure 3. SEM images and EDS elemental maps of freeze-dried Ag-containing chitosan systems. (a) M1, (b) M2, and (c) M3. Red signals in the elemental maps correspond to silver distribution in the analyzed regions.

Table 3. Semi-quantitative EDS elemental composition of freeze-dried Ag-containing chitosan systems.

Sample	C (at.%)	O (at.%)	N (at.%)	Na (at.%)	Ag (at.%)	Ag (wt.%)
M1	77.69	21.32	n.d.	n.d.	0.99	7.71
M2	62.16	n.d.	10.43	24.88	2.54	15.76
M3	68.83	n.d.	25.63	n.d.	5.54	33.52

n.d.: not detected or not reported for the selected mapped region. EDS values correspond to local semi-quantitative analysis and should not be interpreted as bulk composition.

M1 exhibited a lamellar or film-like morphology with surface roughness and dispersed Ag-rich regions. EDS mapping showed the presence of silver distributed over the analyzed region, with 0.99 at.% Ag and 7.71 wt.% Ag. M2 showed a distinct morphology, with rod-like structures and aggregates. EDS analysis indicated the presence of carbon, nitrogen, sodium, and silver, with 2.54 at.% Ag and 15.76 wt.% Ag. Sodium represented 24.88 at.% of the analyzed region. M3 displayed a rough surface with localized Ag-containing aggregates. The mapped region showed 5.54 at.% Ag and 33.52 wt.% Ag.

3.7. Antimicrobial Screening of Ag-Containing Chitosan Systems

The antimicrobial response of the Ag-containing chitosan systems was first evaluated using the original products obtained from the synthesis routes. Representative images are shown in Figure S5. M1 showed limited inhibition, with a visible inhibition halo of approximately 7 mm only against *K. pneumoniae*. M2 produced visible inhibition zones against both bacteria, with diameters of approximately 17 and 13 mm against *K. pneumoniae* and 17 and 20 mm against *S. aureus*. M3 also showed visible inhibition against both bacteria, although the inhibition zones were not quantitatively determined for the original suspension.

The antimicrobial screening was then performed using the freeze-dried Ag-containing chitosan systems. Representative images are shown in Figure 4, and the approximate inhibition halo diameters are summarized in Table 4. After freeze-drying, all systems showed increased inhibition compared with their original form. For *K. pneumoniae*, inhibition halos of approximately 9, 24, and 45 mm were observed for M1, M2, and M3, respectively. For *S. aureus*, the corresponding halos were approximately 30, 45, and 22 mm.

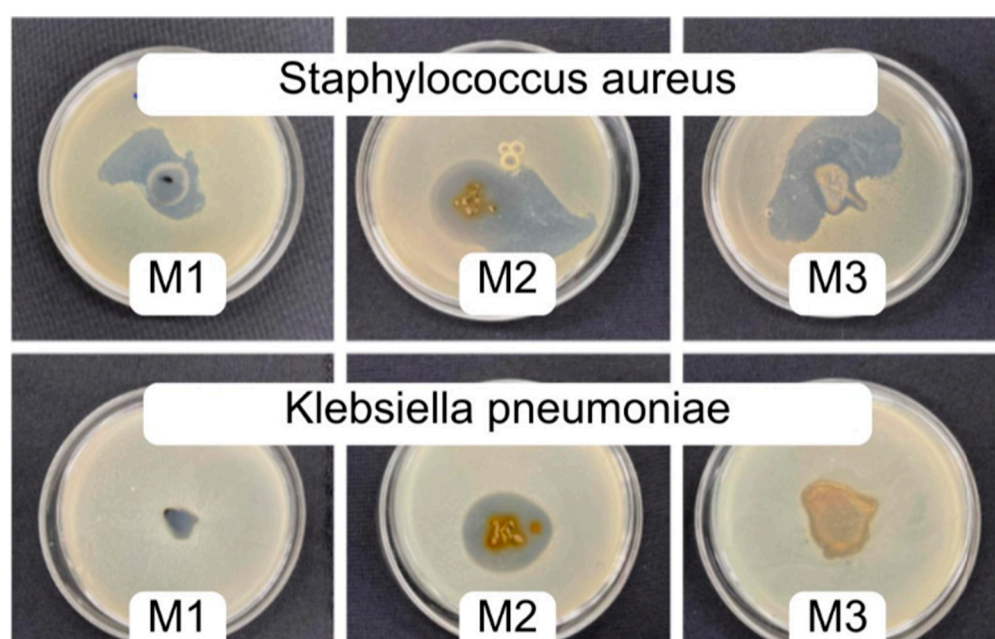


Figure 4. Qualitative antimicrobial screening of freeze-dried Ag-containing chitosan systems. The upper row corresponds to assays against *S. aureus*, and the lower row corresponds to assays against *K. pneumoniae*. M1, M2, and M3 indicate the materials obtained from the three synthesis routes after freeze-drying.

Table 4. Approximate inhibition halo diameters observed for freeze-dried Ag-containing chitosan systems.

Sample	<i>K. pneumoniae</i> (mm)	<i>S. aureus</i> (mm)
M1	9	30
M2	24	45
M3	45	22

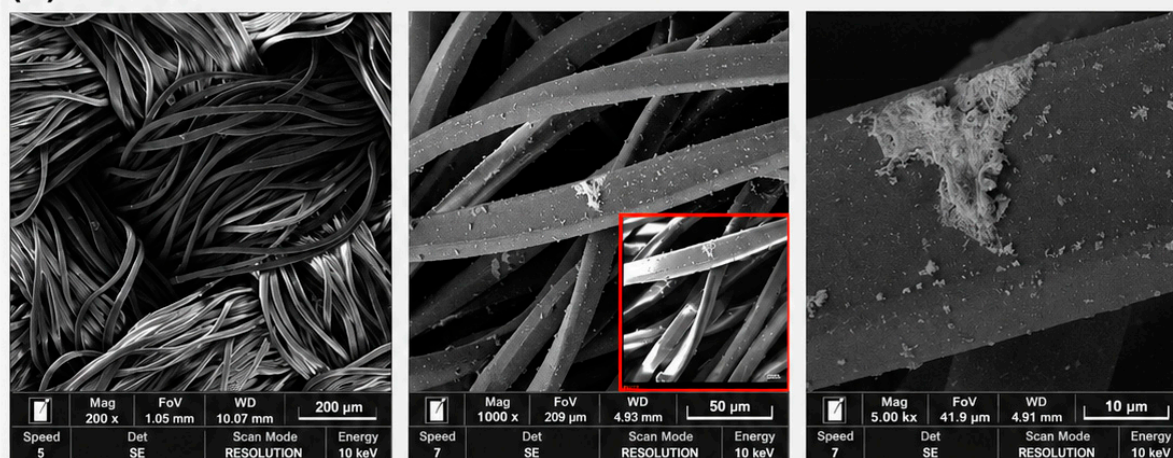
Values correspond to approximate halo diameters obtained from qualitative antimicrobial screening.

3.8. Polyester Functionalization, Silver Deposition, Operational Silver Extraction, and Antimicrobial Response

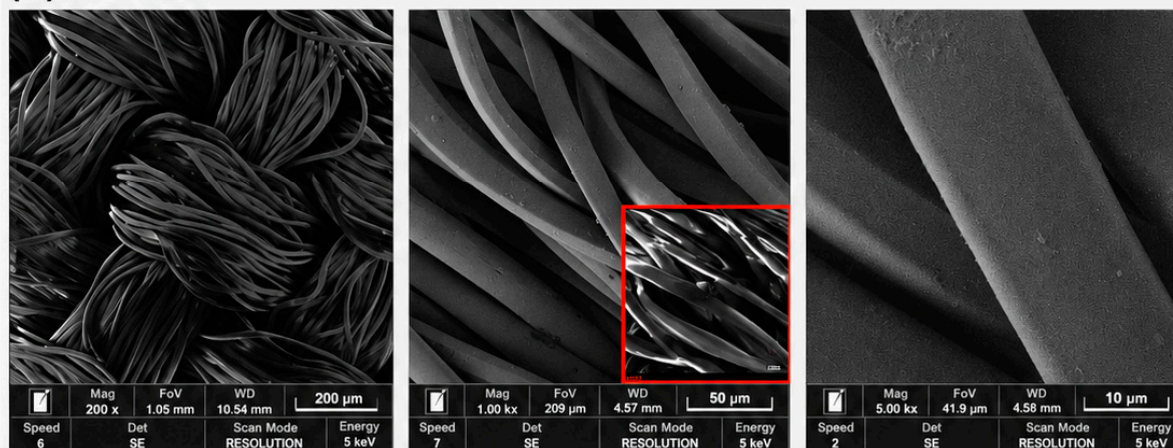
Polyester fabrics were treated with the Ag-containing chitosan systems by exhaustion dyeing at 130 °C for 45 min. SEM/EDS analysis was used to evaluate the presence and distribution of silver on the treated fabrics. Representative SEM images and Ag elemental

maps are shown in Figure 5, and the combined results of silver deposition, operational silver extraction, and antimicrobial response are summarized in Table 5.

(a) PET-M1



(b) PET-M2



(c) PET-M3

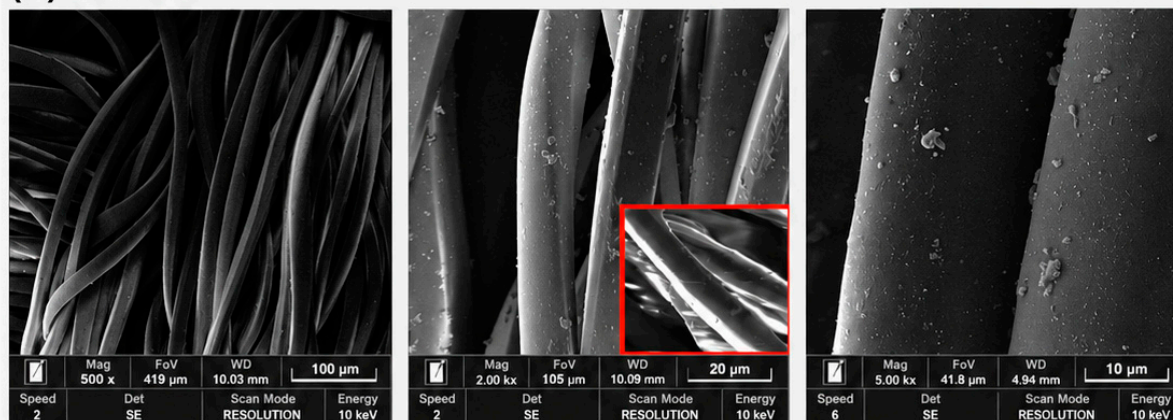


Figure 5. SEM images and EDS elemental maps of polyester fabrics treated with Ag-containing chitosan systems by exhaustion dyeing. (a) PET-M1, (b) PET-M2, and (c) PET-M3. Red signals in the elemental maps correspond to silver distribution on the polyester surface.

Table 5. Silver deposition, operational silver extraction, and qualitative antimicrobial response of polyester fabrics treated with Ag-containing chitosan systems.

Sample	C (at.%)	O (at.%)	N (at.%)	Ag by EDS (at.%)	Ag by EDS (wt.%)	Extracted Ag by AAS (mg L ⁻¹)	Qualitative Antimicrobial Response
PET-M1	70.75	25.74	2.81	0.69	5.43	3.31	No clear inhibition
PET-M2	72.68	24.38	2.83	0.11	0.90	3.89	Weak inhibition
PET-M3	78.48	18.14	3.18	0.20	1.64	29.15	Clear inhibition

EDS values correspond to local semi-quantitative analysis and should not be interpreted as bulk composition. Silver concentrations determined by AAS correspond to the amount of silver extracted into the saline medium after contact with 0.9% NaCl solution under the tested conditions. The antimicrobial response was evaluated qualitatively and should not be interpreted as a standardized quantitative antimicrobial efficiency test.

PET-M1 showed localized Ag-containing regions on the fiber surface, with 0.69 at.% Ag and 5.43 wt.% Ag in the mapped region. PET-M2 showed a more dispersed but low-intensity Ag signal, with 0.11 at.% Ag and 0.90 wt.% Ag. PET-M3 also showed a low amount of silver distributed over the textile surface, with 0.20 at.% Ag and 1.64 wt.% Ag. In all treated fabrics, carbon and oxygen were the predominant elements detected by EDS.

Atomic absorption spectroscopy was used to quantify the amount of silver extracted into the saline medium after contact between the treated polyester fabrics and 0.9% NaCl solution under agitation for 1 h at 37 °C. PET-M1 and PET-M2 showed similar extracted silver concentrations, corresponding to 3.31 and 3.89 mg L⁻¹, respectively. PET-M3 showed a substantially higher extracted silver concentration, corresponding to 29.15 mg L⁻¹.

The antimicrobial response of the treated polyester fabrics was evaluated using an adapted qualitative procedure. Representative images are shown in Figure S6. PET-M1 did not show clear antimicrobial inhibition under the tested conditions. PET-M2 showed weak inhibition, while PET-M3 showed clear inhibition in the qualitative assay.

4. Discussion

4.1. Influence of the Synthesis Route on the Formation of Ag-Containing Chitosan Systems

The three chitosan-assisted synthesis routes produced Ag-containing systems with markedly different optical, structural, morphological, and antimicrobial features. This confirms that small changes in reducing conditions, pH adjustment, reaction temperature, purification, and drying strongly affect the final properties of Ag/chitosan materials. Although all routes were based on previously reported procedures [14–16], their reproduction or adaptation under the present experimental conditions resulted in systems with different degrees of silver reduction, dispersion, matrix contribution, and residual inorganic content.

Among the evaluated routes, M1 showed the most defined UV-Vis absorption band, with λ_{max} close to 400 nm before and after freeze-drying/redispersion. This spectral profile is consistent with the surface plasmon resonance commonly reported for silver nanoparticles dispersed in polymeric or biopolymeric matrices [6,8,10,14]. In practical terms, the higher Absmax and narrower FWHM observed for M1 indicate a stronger and more defined optical response, suggesting that the NaBH₄-assisted route favored the formation of optically active metallic silver domains with lower spectral heterogeneity than the other routes. The blue shift and FWHM decrease after redispersion suggest a change in the dominant detected optical population, possibly associated with partial disruption of larger aggregates or improved redispersion of Ag-containing domains. However, these UV-Vis changes should not be interpreted alone as direct evidence of smaller metallic cores or higher silver concentration. XRD also confirmed the presence of metallic silver in M1, with reflections assigned to the face-centered cubic structure of Ag. Together, UV-Vis and XRD indicate that the NaBH₄-assisted route was the most effective in producing a

structurally and optically defined metallic silver-containing chitosan system under the conditions used in this study.

M2 also showed diffraction peaks assigned to metallic silver, indicating that the two-step chitosan/NaOH route promoted silver reduction. However, the broader and less intense UV-Vis band indicates a more heterogeneous optical response than that observed for M1. This suggests that, although metallic silver was formed, the silver-containing domains were probably more affected by aggregation, matrix interactions, or residual inorganic species. SEM/EDS revealed a high sodium content in the analyzed region, together with rod-like structures rich in inorganic elements. This is an important result because it indicates that, even after centrifugation and washing, residual alkaline or sodium-containing species may remain in the material. Therefore, the biological response of M2 cannot be discussed solely in terms of AgNP formation, since residual inorganic species may also affect the local medium and bacterial growth.

M3 showed the weakest and least resolved UV-Vis response, together with less defined XRD reflections assigned to metallic silver. Although a visible color change was observed during synthesis and Ag was detected by EDS, the combined characterization suggests that M3 did not produce the same level of structurally defined metallic silver observed for M1 and M2. The broad and low-intensity UV-Vis band, as well as the estimated FWHM values after baseline correction, indicate a heterogeneous optical response with possible overlap between silver-containing species and the chitosan matrix. This reinforces the need to describe the obtained products as Ag-containing chitosan systems rather than assuming that all silver is present as well-defined, isolated AgNPs.

4.2. Effect of Freeze-Drying and Redispersion on Dispersion Behavior

Freeze-drying followed by redispersion substantially changed the apparent hydrodynamic size distribution of all Ag-containing chitosan systems. Before freeze-drying, the main DLS peaks were in the submicrometric range, whereas after redispersion the main detected peaks shifted to values below 40 nm. Since the freeze-dried materials were redispersed using the same nominal initial volume of water, this change cannot be attributed to simple dilution. Instead, it indicates that the drying/redispersion process modified the colloidal state of the Ag-containing chitosan systems.

However, DLS data must be interpreted cautiously in Ag/chitosan systems. DLS measures the hydrodynamic diameter of scattering entities in suspension, which may include metallic silver domains, chitosan chains or shells, hydrated polymeric aggregates, residual synthesis components, and particle clusters. In addition, intensity-weighted DLS distributions are strongly biased toward larger scatterers because, under Rayleigh scattering conditions, the scattered intensity scales approximately with the sixth power of particle diameter [20]. Therefore, the apparent shift to smaller hydrodynamic diameters after redispersion should not be interpreted as a physical decrease in the size of metallic silver nanoparticles. A more appropriate interpretation is that freeze-drying followed by sonication changed the dominant detected population, possibly by disrupting larger chitosan-rich aggregates, redistributing Ag-containing domains, or increasing the relative contribution of smaller redispersed species.

The increase in UV-Vis absorbance after redispersion for M1, M2, and M3 is also compatible with changes in dispersion state. Better optical accessibility of Ag-containing domains, partial aggregate disruption, or changes in light scattering after redispersion may contribute to the observed spectral differences. Therefore, freeze-drying/redispersion should be considered an active processing step that changes the physical state of the Ag/chitosan systems, not merely a sample storage procedure.

4.3. Relationship Between Ag-Containing Systems and Antimicrobial Response Before Textile Application

The freeze-dried Ag-containing chitosan systems showed stronger antimicrobial inhibition than the original products, but the response varied according to the bacterial strain and synthesis route. M2 and M3 produced the largest inhibition zones, while M1 showed a more limited response against *K. pneumoniae* but a clear inhibition halo against *S. aureus* after freeze-drying. These results confirm that the synthesized systems had antimicrobial potential before textile application.

Nevertheless, the antimicrobial behavior of these materials cannot be attributed exclusively to silver nanoparticles. AgNP antimicrobial activity is usually associated with Ag⁺ release, membrane damage, oxidative stress, disruption of metabolic pathways, and interactions with proteins and nucleic acids [6–8]. At the same time, chitosan has intrinsic antimicrobial activity related to its polycationic character, interaction with bacterial membranes, modification of permeability, and possible intracellular effects depending on molecular weight, deacetylation degree, and pH [11–13]. In the case of M2, the high sodium content detected by EDS adds another possible contribution, since residual alkaline species may affect bacterial viability or alter the local diffusion environment in agar-based assays.

Therefore, the inhibition zones observed for the Ag-containing chitosan systems should be interpreted as the combined response of a multiphase material composed of silver species, chitosan, and possible residual synthesis components. This interpretation is particularly important because qualitative disk diffusion assays are strongly influenced by diffusion behavior. Materials that release antimicrobial species more easily may generate larger inhibition zones even if they do not contain the highest total amount of silver.

4.4. Limitations of Direct Transfer to Polyester by Exhaustion Dyeing

The main limitation observed in this study was not the formation of Ag-containing chitosan systems, but the interaction between these systems and the polyester surface during exhaustion dyeing. In this context, silver deposition depends on both the Ag/chitosan synthesis route and the textile functionalization strategy. The synthesis route determines the physical state, dispersion behavior, silver-containing domains, residual inorganic content, and chitosan matrix organization of each system, whereas the exhaustion dyeing process determines how these materials interact with the hydrophobic and chemically inert PET surface under high-temperature aqueous conditions. Therefore, the antimicrobial response of the treated fabrics cannot be predicted only from the antimicrobial activity of the original Ag/chitosan systems; it also depends on how much silver-containing material is deposited, how strongly it is retained, and how much silver remains available for release under the assay conditions.

This limitation is consistent with the chemical nature of polyester. Polyethylene terephthalate is hydrophobic and relatively chemically inert, with limited availability of reactive functional groups for spontaneous binding of hydrophilic biopolymers or inorganic nanoparticles [1,17,18]. As a result, the direct application of Ag-containing chitosan systems by exhaustion dyeing may promote partial deposition, but it does not necessarily ensure homogeneous distribution, strong anchoring, wash stability, or long-term antimicrobial performance. In the absence of surface activation, binders, crosslinkers, plasma treatment, or in situ formation on the fiber, Ag/chitosan materials may remain weakly associated with the polyester surface. Such weakly retained species can contribute to short-term antimicrobial activity if silver is readily released, but they may also be more susceptible to removal during washing or repeated use. Previous studies have shown that more efficient incorporation of silver-based materials into textile substrates often requires in

situ formation, surface activation, plasma treatment, binders, crosslinkers, or polymeric matrices capable of improving adhesion and controlling release [5,17–19].

The comparison with recent textile functionalization strategies highlights this point. Ribeiro et al. used organo-matrices to stabilize AgNPs on polyester and obtain controlled antimicrobial performance [17]. Montes-Hernandez et al. demonstrated that the in situ formation of AgNPs on textile fibers depends strongly on fiber type and surface properties, with polyester showing lower silver incorporation than natural fibers [18]. Dumas et al. showed that a polysaccharide coating can increase silver loading and improve antimicrobial activity compared with direct AgNP incorporation on fabric [19]. These studies support the interpretation that the textile substrate and anchoring strategy are decisive for antimicrobial finishing performance. Thus, for polyester, the bottleneck is not only the antimicrobial activity of the Ag-containing system itself, but also the interfacial compatibility between the hydrophilic chitosan-based material and the hydrophobic PET surface.

4.5. Operational Silver Extraction and Antimicrobial Response of Treated Polyester Fabrics

The AAS results showed that PET-M3 extracted a much higher concentration of silver into the saline medium than PET-M1 and PET-M2. This result helps explain why PET-M3 showed the clearest antimicrobial response despite not presenting the highest Ag content by EDS. In antimicrobial textile systems based on silver, biological activity is often more closely related to the availability and release of silver species than to the total amount of silver detected on a selected surface region [6–8,18,19]. Therefore, the higher silver concentration measured for PET-M3 in the extraction medium suggests greater availability of releasable silver species under the tested conditions.

The comparison among PET-M1, PET-M2, and PET-M3 illustrates how the interaction between synthesis route and textile functionalization affected performance. PET-M1 showed the highest local Ag content by EDS among the treated fabrics, but only 3.31 mg L^{-1} of extracted Ag and no clear antimicrobial inhibition. This suggests that the silver-containing material deposited from M1 may have been locally present on the fiber surface but was not sufficiently available to produce inhibition under the qualitative antimicrobial assay. PET-M2 showed low Ag by EDS, low extracted Ag, and weak inhibition, indicating limited transfer and limited silver availability after exhaustion dyeing. PET-M3, in contrast, showed low Ag by EDS but the highest extracted Ag concentration and the clearest antimicrobial response, indicating that the Ag-containing species transferred from this route were more available for release into the surrounding medium. Thus, the antimicrobial behavior of the treated fabrics was governed not only by the amount of silver detected on the surface, but by the balance between deposition, retention, and release of silver species.

However, the same behavior that favors short-term antimicrobial activity may limit wash stability. A higher concentration of extractable silver may indicate greater availability of antimicrobial silver species, but it may also suggest weaker retention of Ag-containing material on the polyester surface. Since durability against washing or repeated use was not evaluated in this study, the antimicrobial response observed for PET-M3 should be considered preliminary. Silver- and nanosilver-containing textiles may show antimicrobial efficacy associated with silver availability, but the extent of silver release or loss during washing depends strongly on the loading method, attachment strategy, and textile substrate [21]. In this context, wash-durable antimicrobial fabrics usually require more effective anchoring strategies, such as in situ formation of AgNPs or coating approaches capable of retaining silver-containing species on the fiber surface after repeated laundering [22]. For this reason, the treated fabrics should not be described as durable antimicrobial textiles.

The mismatch between EDS-detected Ag and antimicrobial response also reinforces the limitations of using local surface composition as the only indicator of functional performance. EDS provides local, semi-quantitative information from selected regions of the fabric, whereas AAS reflects the amount of silver extracted into the medium under defined conditions. These techniques therefore provide complementary information: EDS indicates whether silver-containing species were deposited on the textile surface, while AAS provides information about silver availability in the surrounding medium.

Another important point is that the antimicrobial assay used for the treated fabrics was interpreted qualitatively. Although the procedure was adapted from a dynamic contact approach, the results were not expressed as standardized log reduction or percentage reduction values. Therefore, the assay is useful for screening differences among PET-M1, PET-M2, and PET-M3, but it should not be interpreted as a quantitative certification of antimicrobial textile performance. This limitation is consistent with the overall objective of this study, which was to evaluate synthesis-to-textile transferability rather than to validate a finished commercial antimicrobial fabric.

4.6. Implications for Synthesis-to-Textile Transferability

Overall, the results demonstrate that successful synthesis of Ag-containing chitosan systems does not guarantee efficient antimicrobial finishing of polyester by exhaustion dyeing. The three routes produced materials with antimicrobial potential before textile application, but their transfer to polyester was limited and synthesis-dependent. This finding is central to the concept of synthesis-to-textile transferability. A colloidal or polymer-stabilized nanoparticle system may show promising optical, structural, or antimicrobial properties in suspension or as a dried powder, but these properties may not be preserved after application to a hydrophobic textile substrate.

The present study therefore does not support a claim of optimized antimicrobial polyester finishing. Instead, it identifies critical barriers that must be addressed for future development: purification of residual synthesis components, control of dispersion state before textile application, evaluation of operational silver extraction, and incorporation of anchoring strategies suitable for polyester. Future studies should consider surface activation of polyester, plasma treatment, alkaline hydrolysis, binder-assisted finishing, polydopamine-mediated adhesion, in situ silver reduction on the fabric, or biopolymer coating strategies, since these approaches may improve the retention of silver-containing species and support wash-durable antimicrobial performance [22]. In addition, standardized quantitative antimicrobial assays and washing durability tests are required to confirm whether the observed inhibition can be translated into a robust textile functionality.

From the perspective of wash stability, the present results indicate that deposition and antimicrobial activity must be interpreted together with silver release. A fabric with low release may show poor antimicrobial performance even if silver is locally detected by EDS, whereas a fabric with high release may show stronger short-term inhibition but potentially lower retention during washing. Therefore, the interaction between Ag/chitosan synthesis and polyester functionalization creates a trade-off between antimicrobial availability and retention. Future optimization should aim to increase silver deposition and fiber anchoring while maintaining controlled silver release, so that antimicrobial activity is preserved after laundering.

Thus, the main contribution of this work is a critical evaluation of the direct transfer of reported Ag/chitosan synthesis routes to polyester finishing. The findings show that the synthesis route influences not only Ag-containing system formation, but also redispersion behavior, silver deposition, operational silver extraction, and antimicrobial response after

textile application. This reinforces the need to evaluate nanoparticle synthesis and textile functionalization as interconnected steps rather than independent processes.

5. Conclusions

Three chitosan-assisted silver-containing systems were reproduced or adapted from reported synthesis routes and evaluated for antimicrobial polyester functionalization by exhaustion dyeing. The synthesis route strongly influenced the optical, structural, morphological, and antimicrobial properties of the obtained materials. The NaBH_4 -assisted route produced the most defined plasmonic response and clear XRD reflections of metallic silver, whereas the NaOH -assisted routes resulted in broader optical responses and, in the case of M2, residual sodium-containing structures. Drying/freeze-drying followed by redispersion also changed the apparent hydrodynamic populations of all systems, indicating that this step affected the colloidal state of the Ag-containing chitosan materials.

Although all systems showed antimicrobial potential before textile application, their transfer to polyester was limited. SEM/EDS confirmed silver deposition on the treated fabrics, but the detected silver contents were low and locally distributed. Among the treated fabrics, PET-M3 showed the clearest antimicrobial response, which was associated with the highest silver concentration detected in the saline extraction medium rather than with the highest surface silver content by EDS. These results indicate that the qualitative antimicrobial response was more closely related to the availability of extractable silver species under the tested conditions than to local silver deposition alone. A direct quantitative relationship between hydrodynamic size and the amount of silver deposited on polyester could not be established from the present results. The DLS values represent apparent hydrodynamic populations in suspension and are influenced by the chitosan matrix, solvation layer, aggregation state, and redispersion behavior, whereas Ag deposition on polyester was evaluated by local semi-quantitative EDS analysis. Moreover, the observed trends were not monotonic: the system with the largest apparent hydrodynamic diameter did not produce the highest local Ag deposition on polyester, and the fabric with the highest extractable silver concentration was not the one with the highest Ag content by EDS. Therefore, hydrodynamic size, silver deposition, silver release, and antimicrobial response should be interpreted as complementary but not directly proportional parameters.

Overall, the direct application of Ag-containing chitosan systems to polyester by exhaustion dyeing did not result in a robust or optimized antimicrobial textile, and the textile performance could not be predicted from hydrodynamic size alone. The findings demonstrate that nanoparticle formation in solution does not necessarily ensure efficient deposition, retention, or antimicrobial activity on polyester fibers. Therefore, future development of Ag/chitosan-based polyester finishes should include improved purification, dispersion control, operational silver extraction studies, quantitative antimicrobial assays, standardized washing durability tests, post-washing silver quantification, and specific anchoring strategies for polyester, such as surface activation, binder-assisted finishing, or in situ silver formation on the fabric.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/appliedchem6030051/s1>, Figure S1. Visual appearance of the Ag-containing chitosan systems obtained by the three synthesis routes. M1: chitosan/ NaBH_4 -assisted route; M2: two-step chitosan/ NaOH route; M3: one-pot chitosan/ NaOH route. Figure S2. Visual appearance of polyester fabrics after exhaustion dyeing with the Ag-containing chitosan systems. PET-M1, PET-M2, and PET-M3 correspond to fabrics treated with the products obtained from M1, M2, and M3, respectively. Figure S3. Number-weighted DLS size distribution profiles of Ag-containing chitosan systems before and after drying/freeze-drying and redispersion. (a) M1, (b) M2, and (c) M3. Figure S4. TGA curves of freeze-dried Ag-containing chitosan systems. (a) M1, (b) M2, and (c) M3.

The analyses were performed under argon atmosphere from 25 to 800 °C at 10 °C min⁻¹. Figure S5. Qualitative antimicrobial screening of the original Ag-containing chitosan systems before freeze-drying. Assays were performed by disk diffusion against *K. pneumoniae* and *S. aureus*. Figure S6. Qualitative antimicrobial assay of polyester fabrics treated with Ag-containing chitosan systems. The control corresponds to bacterial growth in the absence of treated fabric. PET-M1, PET-M2, and PET-M3 correspond to fabrics treated with the products obtained from M1, M2, and M3, respectively. Figure S7. Full EDS spectra corresponding to the analyzed regions of the freeze-dried Ag-containing chitosan systems. (a) M1, (b) M2, and (c) M3. The spectra support the semi-quantitative elemental composition values reported in Table 3 of the main manuscript.

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Abbreviations

The following abbreviations are used in this manuscript:

AAS	Atomic absorption spectroscopy
AgNPs	Silver nanoparticles
DLS	Dynamic light scattering
EDS	Energy-dispersive X-ray spectroscopy
FWHM	Full width at half maximum
LSPR	Localized surface plasmon resonance
PET	Polyethylene terephthalate
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
UV-Vis	Ultraviolet-visible spectroscopy
XRD	X-ray diffraction

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