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Antibacterial and eco-friendly textile finishes: the potential of natural organic acids

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Abstract

While cotton fabric is comfortable to wear, it is also a suitable substrate for bacterial growth. To prevent this, various antibacterial treatments are usually implemented during the finishing process. This study investigates the development of antibacterial cotton fabrics by testing different natural organic acids, namely caffeic acid (CA), gallic acid (GA), trans-ferulic acid (tFA), lactic acid (LA), L-ascorbic (L-AsA) and tartaric acid (TA), against *Staphylococcus aureus* and *Escherichia coli* according to the ASTM E2149-2013 standard method. The results indicated that the LA-, L-AsA- and TA-treated fabrics inhibited 95% more bacterial growth than the untreated cotton. To improve the adhesion of antibacterial agents to cotton fabrics and their wet-washing and dry-cleaning fastness, the three selected organic acids were combined with bio-based polymers to develop sustainable antibacterial coatings on cotton samples. The treated fabrics' surface morphology and chemical composition were confirmed using SEM and FT-IR analyses. The antibacterial efficiency of the best-performing samples was further tested after the wet-washing and dry-cleaning. This research can lead to the development of a novel dry-cleaning-resistant and efficient antibacterial, eco-friendly cotton fabric, and provides a viable and promising prospect to produce the same on an industrial scale.

Keywords Antibacterial textile, Organic acids, Textile functionalisation, Bio-based chemicals, Eco-friendly finishing

1 Introduction

Textiles today extend far beyond their traditional role of providing physical coverage; they are increasingly designed to deliver advanced functionalities tailored to industrial, medical, and everyday applications. Functional or "smart" textiles can exhibit properties such as flame retardancy, water repellence, electroconductivity, and antimicrobial activity, offering solutions that enhance safety, comfort, and performance [20, 36, 37, 44, 45, 50, 51]. Among these, antimicrobial functionality is of particular importance due to its critical role in hygiene and infection prevention. Some previous studies have focused on antibacterial cellulose-based fabrics that have potential applications in various sectors [53]. The size of the global textile market was USD 2,010.76 billion in 2024 (Textile

Market Size 2024), with the demand for textile fibres expected to rise at an annual rate of about 3% until 2030 [13] and the forecasted fibre consumption to reach 160 million tons by 2050 [26].

Antimicrobial textiles have gained broad relevance in healthcare, sportswear, and public-use contexts. They are employed in wound dressings, surgical gowns, hospital linens, and masks to minimize microbial contamination and hospital-acquired infections [16]. In sportswear and activewear, such finishes help prevent odor formation and skin irritation caused by bacterial proliferation [5]. Beyond personal use, antimicrobial fabrics are used in home furnishings, air filtration, and transport interiors, where microbial control extends product safety and lifetime [4]. The COVID-19 pandemic further reinforced global demand for functional coatings that combine antimicrobial efficacy with sustainability [29, 53].

In this context, *organic acids (OAs)* represent an emerging class of bio-based, antimicrobial candidates. These compounds are naturally present in foods and plants, are biocompatible, and have well-documented antimicrobial properties [1, 9, 10].

Previous studies have primarily focused on the direct application of organic acids to fabrics, leading to limited wash durability. To overcome this lack, our study proposes an innovative combination of selected OAs with water-based, bio-based polymeric binders to enhance adhesion to the textile substrate while preserving antimicrobial activity.

Furthermore, the antibacterial potential of selected natural organic acids (OAs) as eco-friendly finishing agents for cotton fabrics is here investigated, to evaluate both their efficacy against common pathogens and their resistance to maintenance procedures such as laundering and dry-cleaning. This strategy represents a sustainable and industrially scalable alternative to conventional synthetic antimicrobial coatings and addresses a significant gap in the literature concerning the long-term performance and environmental compatibility of OA-based textile treatments.

In fact, cotton is an integral part of everyday life due to its valuable qualities, including permeability, flexibility, softness, and strength, which make it relevant in new applications in the health, fitness and hygiene sectors (e.g., wound healing, laboratory equipment, sportswear, home and hospital linen and underwear). However, because of their porous nature and capacity to absorb moisture, cotton fibres are prone to microbial growth, which can lead to allergies, unpleasant odours and hospital-acquired diseases [7]. Thus, to overcome these problems, a variety of antibacterial agents, such as metal oxides, inorganic salts, halogens, polyguanidine, oxidising agents, chitosan, onium salts, antibiotics, heterocyclics with anionic groups, amines, nitro compounds, formaldehyde derivatives, urea and related compounds and quaternary ammonium salts, have already been integrated into the textile manufacturing process [6, 22, 30, 31, 40, 53, 57].

However, most of these employed agents have led to phenomena of toxicity or allergic reactions in humans and are not environmentally friendly [2, 9, 14, 39, 55]. Hence, combined with the rising demand for sustainable products driven by consumers, the need to develop antimicrobial textiles using naturally occurring and non-toxic substances is growing, and different kinds of compounds are being explored for this purpose. For this reason, plant extracts (e.g. lavender, aloe vera, thyme, clove, and oregano), essential oils and animal products (e.g., honey and chitosan), as well as natural dyes, pigments and mordants are currently being ed for their antimicrobial capabilities [4, 5, 16, 17, 33].

Organic acids, in particular, are a class of compounds extremely diverse, and although the antibacterial activity and the possible mechanism of action of many of them have already been discussed in previous works [1], evidence regarding their efficacy in the context of textiles is still poor. Their activity may depend on a well-known dissociation phenomenon that occurs once they diffuse into the bacterial cell, where the generation of ions determines mechanisms of cytotoxicity and pH alterations. Bacteria try to counteract these phenomena by extruding protons, which results in an adenosine triphosphate (ATP) depletion linked to the pump activation and, finally, in cell death [11, 38, 41, 48]. As a consequence, the antibacterial activity of these weak acids is related to their dissociation equilibria, so to their pKa values, which range between 3 and 5, approximately [59]. The described mechanism is illustrated in Fig. 1.

Recent work highlights the relationship between pKa and microbial inhibition through acid diffusion mechanisms [15]. Additionally, researchers explored how the pKa of organic acids impacts antimicrobial performance when combined with biopolymeric matrices such as chitosan on textile substrates [56].

These natural compounds are readily available, safe for the environment, and inexpensive [10, 18]. In some cases, they can be obtained from by-products or biotechnological processes, making them good candidates for achieving more sustainable textile functionalisation.

Specifically, the analysed OAs are (Fig. 2): (i) caffeic acid (3,4-dihydroxy cinnamic acid; CA), which is a hydroxycinnamate and phenylpropanoid metabolite and the most abundant phenolic acid that can be found in all plant tissues and in a precursor for lignin [35]; (ii) gallic acid (3,4,5-trihydroxybenzoic acid; GA), which is a phenolic compound found both in a free state and as a constituent of tannins in several fungi, land plants and

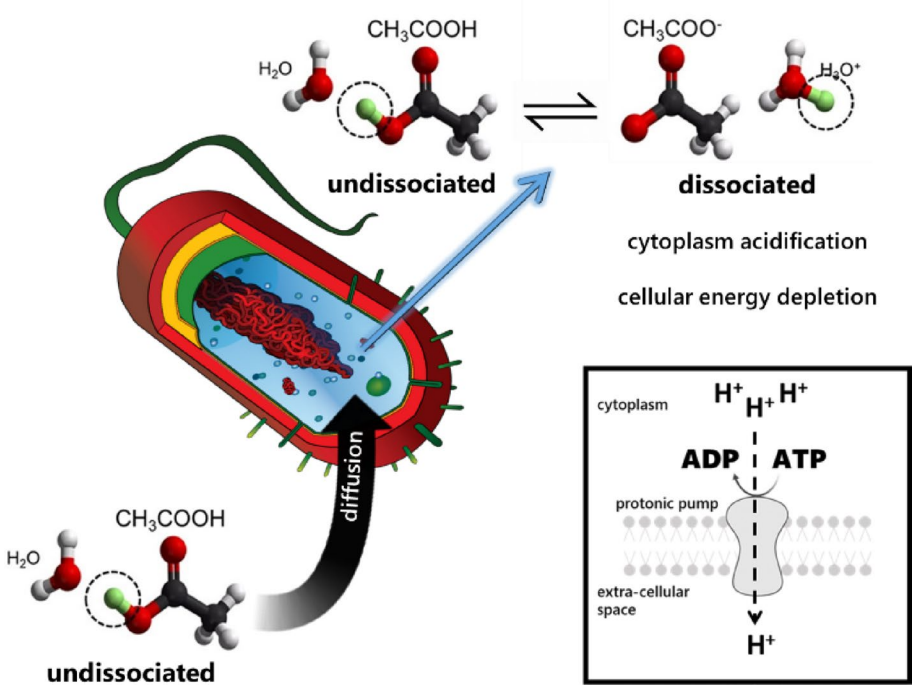

Fig. 1 Schematic mechanism of the antibacterial action of OAs. The undissociated form diffuses into the bacterial cytoplasm, where dissociation occurs, and the derived protons lead to the lowering of the pH and depletion of cellular energy (due to proton pump activation)

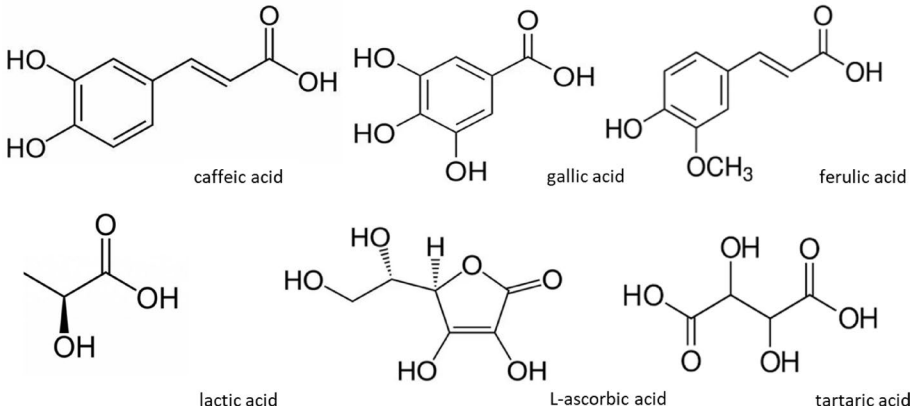

Fig. 2 Chemical structures of the selected OAs

oak species [54]; (iii) trans-ferulic acid (trans-4-hydroxy-3-methoxycinnamic acid; tFA), which is the trans isomer of ferulic acid that, with dihydro ferulic acid, forms the main component of lignocelluloses [19]; (iv) lactic acid (2-hydroxypropanoic acid; LA), which is produced in large quantities through microbial fermentation, employed in various sectors, is naturally present in many foods and is one of the principal metabolic intermediates in most living organisms [49]; (v) L-ascorbic acid (L-AsA), also known as vitamin C, which is naturally found in many plants and used as an essential food supplement and additive due to its strong antioxidant effect [28]; and (vi) tartaric acid (2,3-dihydroxysuccinic acid; TA), or grape acid, which is the primary OA present in grapes (*Vitis vinifera L.*) and is widely employed as an acidulant and preservative agent in the food and wine industries [23].

All these acids are currently employed in the food industry, underscoring their safety for human health and action against food-spoiling bacteria and fungi. In this regard, diverse antimicrobial studies were performed with the selected OAs and their derivatives in various sectors, such as pharmacology and food packaging [3, 21, 27, 34, 46].

From the literature, it is known that only a few studies have been published on the use of OAs for fabric functionalisation, specifically of L-AsA on cotton [12], which suggested a mechanism of crosslinking between L-AsA and cellulose, achieved simply by adding citric acid, a well-known crosslinker for cellulose. A few works investigated the interactions between cellulose and OAs [25, 61]. The results suggested interactions involving carboxyl groups of the acids in hydrogen bonding, electrostatic interactions, and van der Waals forces.

Furthermore, the previously mentioned acids have been incorporated into various bio-based matrices to develop innovative, eco-friendly textile finishing treatments that enhance washing fastness and improve the performance of treated fabrics, including their durability over multiple maintenance cycles. The reactions of OAs with common functional groups in biobased polymer binders, such as carboxylic acids or isocyanates [42], can be included in many textile polymers, resulting in biocidal behavior. The bio-based polymer binders that are used as crosslinking agents were selected considering the risks of formaldehyde and the restrictions on using N-methylol reagents in the development of zero formaldehyde-containing reactants [32]. Due to global trends favouring enhanced sustainability, there has been significant interest in utilising natural, biodegradable, and renewable raw materials in textile finishing processes. This has created the

need to develop bio-based finishes for natural substances manufactured using renewable biological sources that offer longevity and can rival those derived from fossil sources [43].

Accordingly, the present study investigates the antibacterial properties and washing durability of cotton fabrics finished with selected OAs, both alone and in combination with polymeric and polycarboxylic binders. Surface morphology and chemical interactions were characterised by SEM and FT-IR analyses to elucidate the nature of OA–cellulose interactions. This eco-sustainable approach aims to demonstrate an effective, formaldehyde-free finishing route for developing durable, bio-based antibacterial textiles with improved environmental compatibility and industrial applicability.

2 Materials and methods

2.1 Materials

Cotton fabrics (ISO Single-Fiber Standard Adjacent Cotton 105-F02; plain weave fabric with a mass per unit area of 110.75 g/m^2, supplied by Testfabrics Inc., West Pittston, PA, USA) were conditioned under standard atmospheric pressure at 65 ± 4% and relative humidity (RH) at 20 ± 2° C for at least 24 h before all the experiments.

The selected OAs (Fig. 2) were caffeic acid (> 98%, CAS No. 331-39-5), trans-ferulic acid (99%, CAS No. 537-98-4), gallic acid (97.5–102.5% titration, CAS No. 149-91-7), lactic acid (ACS reagent, ≥ 85%, CAS No. 79-33-4), L-ascorbic acid (ACS reagent, CAS No.50-81-7) and tartaric acid (99%, CAS No.87-69-4). All the acids were supplied by Sigma-Aldrich and used as received without further purification.

Citric acid (CitA; Sigma Aldrich 251275 Citric acid, ≥ 99.5%, ACS reagent, used at 6% w/v), Nearcoat BB-AC (Nbbac; Nearchimica, Italy, used at 10% w/v), Vision Sugar 4.0 (VS4; F.T.R. S.r.l., Italy, used at 10% w/v) and Pluvion Dry 2030 BS (PD; F.T.R. S.r.l., Italy, used at 10% w/v) were selected as bio-based crosslinkers to immobilise the OAs on cotton samples.

2.2 Preparation of the functional formulations

The OAs were dissolved in distilled water at 5% and 10% wt/vol. The formulations were prepared in the presence of OAs alone or OAs and biobased polymer binders, and the pH of the solutions with biobased polymer binders was adjusted to 5.5 ± 0.2 using sodium hydroxide (0.1 mol/L) or a sodium acetate/acetic acid buffer solution. Only in the case of citric acid (CitA), sodium hypophosphite (SHP) was added (with a CitA/SHP molar ratio of 1:1) as an effective catalyst for the esterification reaction of cellulose with 2-hydroxypropane-1,2,3-tricarboxylic acid.

Figure 3 illustrates the hypothesised molecular-level interactions among cotton cellulose, bio-based polymeric binders, and OAs.

The scheme summarises the main interactions expected to occur during the functionalisation process, namely, hydrogen bonding between polymeric binders and the carboxyl or hydroxyl groups of the OAs and hydroxyl groups of cellulose; esterification reactions between the carboxylic groups of the OAs or binders (e.g., citric acid, polycarboxylic matrices) and the hydroxyl groups of cellulose under curing conditions, resulting in partial covalent cross-linking; network formation in which the bio-based binder acts as a matrix, embedding OA molecules through both hydrogen bonds and van der Waals forces, thereby improving their retention and washing durability.

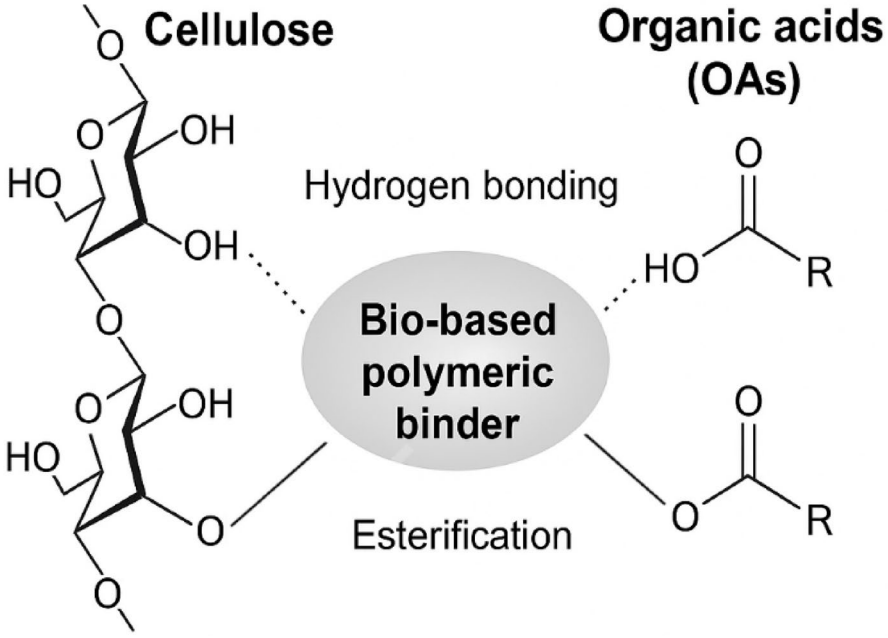

Fig. 3 Scheme of the main interactions during the functionalisation process

The selected OAs were ed at two different concentrations, 10% and 5% wt/vol, in aqueous solution. The initial concentration of 10% wt/vol was chosen based on literature precedent from food safety and biomedical studies, where it demonstrated consistent antimicrobial efficacy. For example, [46] and Popelka et al. [34] reported effective inhibition of *E. coli* and fungal strains using organic acids, including lactic and ascorbic acid, at concentrations ranging from 5% to 10% wt/vol. This concentration was used in preliminary screenings to assess the maximum antibacterial potential of each acid. Subsequently, a reduced concentration of 5% wt/vol was selected to evaluate the lowest effective dosage that still ensured bacterial reduction. This approach aimed to balance biological activity with considerations for cost-efficiency and material usage, aligning with the study's objective of developing an industrially viable, sustainable, and antimicrobial finishing. Similarly, bio-based polymeric binders were incorporated into the formulations at a standard concentration of 10% wt/vol. This concentration was derived from manufacturer technical datasheets and common practices in textile coating applications, guaranteeing appropriate viscosity and film formation without excessive build-up. Combining these polymeric additives with OAs aimed to improve adhesion to the cotton substrate and enhance retention during washing and dry-cleaning simulations, thus reflecting a realistic scenario for industrial upscaling.

2.3 Preparation of textile fabrics

The fabric samples, which were cut into 10 × 4 cm stripes (warp direction) with an average weight of 0.5 g, were padded into the acid solutions until soaked (60 s) through gentle stirring. The fabrics were drained for 60 s by being held with a tweezer before being weighed. Next, they were dried at 105 °C for 10 min and cured at 150 °C for 5 min in the oven ([8, 24, 58, 60]Verbič et al. [52]). Once cooled, the samples were stored at 20 °C and 65% RH for at least 24 h before being weighed and used for the tests.

Table 1 Wet pick-up and dry solid add-on of the OAs used for the cotton samples (assigned codes in brackets)

Active compound	Wet pick-up (%)	Add-on (%)
Lactic acid (LA) 10%	175	3.5
L-Ascorbic acid (L-AsA) 10%	182	14
Tartaric acid (TA) 10%	182	13.5
Lactic acid (LA) 5%	165	2.4
L-Ascorbic acid (L-AsA) 5%	180	7.4
Tartaric acid (TA) 5%	176	6.8

Table 2 Composition and wet pick-up of bio-based formulations on cotton samples

Wet pick-up (%)	Organic acids (OAs)			
Bio-based crosslinkers	**-**	**LA (5%)**	**L-AsA (5%)**	**TA (5%)**
Citric acid (CitA)	78.6	79.0	79.3	81.3
Nearcoat BB-AC (Nbbac)	73.0	76.5	79.0	79.5
Pluvion Dry 2030 BS (PD)	65.0	78.0	77.0	77.0
Vision Sugar 4.0 (VS4)	74.0	74.8	76.9	76.0

Table 3 Composition and dry solid add-on of bio-based formulations on cotton samples

Bio-based crosslinkers	Organic acids (OAs)			
	-	**LA (5%)**	**L-AsA (5%)**	**TA (5%)**
Citric acid (CitA) 6%	5.6	8.8	9.4	6.5
Nearcoat BB-AC (Nbbac)	1.5	4.5	7.0	6.5
Pluvion Dry 2030 BS (PD)	2.2	4.0	5.0	5.0
Vision Sugar 4.0 (VS4)	2.3	5.4	7.4	6.6

The wet pick-up and dry solid add-on values (x) reported in Table 1 were calculated using Eq. (1):

$$x = \frac{W_f - W_i}{W_i} \times 100 \tag{1}$$

Subsequently, according to the combination reported in Table 2, bio-based commercial polyacrylates, namely Vision Sugar 4.0 (VS4, 10% wt/vol), Pluvion Dry 2030 BS (PD, 10% wt/vol), Nearcoat BB-AC (Nbbac, 10% wt/vol), and citric acid (CitA, 6% wt/vol) were combined separately with LA, L-AsA or TA (ranging among 5 and 10%) and stirred vigorously until limpid solutions were obtained as reported in the previous paragraph. Next, these solutions were used to impregnate the cotton samples (25 cm × 30 cm) that were passed through a two-roll laboratory padder (Werner Mathis, Zurich, Switzerland), working with a 2 bar nip pressure, to achieve a 70% wet pick-up. After drying at 95 °C for 5 min, the textile samples were cured at 170 °C for 2 min in a gravity convection oven. Once cooled, the clear-coated samples were stored at 20 °C and 65% RH for at least 24 h before the experiments were conducted. The wet pick-up and add-on values, calculated according to Eq. (1), are reported in Tables 2 and 3 after each treatment.

2.4 Durability after wet and dry-cleaning

The durability of the coatings was evaluated according to modified ISO 105-C06:1999 (Standard testing method for colour fastness to washing) and ISO 105-X05:1999 (Standard testing method for colour fastness to organic solvents). For wet cleaning, the samples were washed using two types of surfactants: an ionic detergent (ECE-98 type

A without phosphate, supplied by Ausiliari Tessili S.r.l., Italy) at 4 g/L and a non-ionic surfactant (Triton™ X-305, supplied by Sigma Life Science) at 5 g/L. The washing process for each cycle was performed according to EN ISO 105 – C06:1999, in a Hanau Linitest machine at 40 °C for 30 min. After that, the washed samples were rinsed under tap water and dried for 25 min in an oven at 37 °C before other tests. This standard method aims to simulate domestic and commercial washes to assess the durability of coatings after laundering. The bath ratio (grams of water for each gram of textile sample) was 50:1. Ten stainless steel balls were added to the metallic vessel to simulate washing mechanical stress.

The dry-cleaning process was conducted in a Linitest machine (Atlas, USA), using a procedure with tetrachloroethylene, supplied by Sigma-Aldrich, as the solvent at 30 °C for 10 min, with a bath ratio 40:1, according to ISO 105-X05:1999. Once the experiment was over, the samples were extracted, rinsed and air-dried under the fume hood to avoid solvent dispersion for at least 24 h.

2.5 Characterisations

2.5.1 Antibacterial test

The bacterial strains were obtained from the American Type Culture Collection (ATCC): Gram-positive *Staphylococcus aureus* ATCC 6538 and Gram-negative *Escherichia coli* ATCC 11,229. The primary cultures were prepared using lyophilised bacteria kits supplied by KwikStik™; the suspensions were put into a petri dish containing 20 mL of yeast extract agar for microbiology (Sigma-Aldrich 01497 –500 g, suitable for *E. coli* and *S. aureus*).

The antibacterial activity of the OA solutions and the acid-treated cotton samples was evaluated according to ASTM E2149-2013 "Standard test method for determining the antimicrobial activity of antimicrobial agents under dynamic contact conditions". The chosen bacteria, *E. coli* and *S. aureus*, were representative of Gram-negative and positive bacteria, respectively. The test cultures were created by suspending the bacteria in a nutrient broth (buffered peptone water for microbiology, VWR Prolabo® Chemicals). The antibacterial tests were performed by diluting the bacterial inoculum in a pH 7.2 ± 0.1 buffer solution (Honeywell Fluka™, 0.25 M KH_2PO_4, with fungicide) to yield a concentration of $1.5–3.0 \times 10^5$ CFU (colony-forming unit)/ mL (working dilution). For each test, 0.5 g of fabric was immersed in 25 mL of the working dilution in a flask, which was then shaken for an hour (± 5 minutes) at 190 rpm at room temperature. Serial dilutions were carried out with the cited buffer until a concentration of 150–300 CFU/mL was achieved for plating: 1 mL of the liquid was added to 15 mL of yeast extract agar. After incubation at 37 °C for 24 h, the surviving cells were counted using the plate count method.

The antibacterial activity is expressed as the percentage of bacterial reduction based on contact with the test specimen, compared to the number of bacterial cells that survive after contact with the control. It is calculated using Eq. (2):

$$\%\,\text{reduction}\,\left(\text{CFU}\,\text{ml}^{-1}\right) = \frac{\text{B} - \text{A}}{\text{B}} \times\ 100 \tag{2}$$

Here, A is CFU/ml after contact (end test), and B is CFU/ml at zero contact time (used as reference).

2.5.2 The tests were done in triplicate

A one-way ANOVA followed by Tukey's multiple comparisons test was applied to compare the bacterial reduction values, with p-values < 0.05 (unless otherwise stated).

2.6 Scanning electron microscopy

The surface morphology of the treated and untreated fabrics was compared using an EVO 10 scanning electron microscope (Carl Zeiss AG, Oberkochen, Germany) with an acceleration voltage of 20 kV, a current probe of 100 pA and a working distance of about 30 mm. The fabric samples were mounted on aluminium specimen stubs and sputter-coated with a 20 nm thick gold layer in the presence of rarefied argon using a Quorum Q150RES Plus Sputter Coater.

2.7 Contact angle

The water contact angle was measured with a 10 µL deionised water droplet at ambient temperature with an EasyDrop optical contact angle meter (Krüss Scientific GmbH, Hamburg, Germany). The contact angle values reported are averages of five measurements made on different areas of the textile surface. All measurements for all surfaces were within ± 2.0° of the averages. The drop absorption time evaluations were conducted with deionised water to evaluate the wettability of the analysed fabrics. The more significant the measured contact angle, the more hydrophobic the surface, as the droplet's surface tension minimises the area in contact with the cotton surface.

2.8 Infrared spectroscopy

The FT-IR analysis was carried out using the attenuated total reflection (ATR) technique in the range of 4000–650 cm^{-1} with 32 scansions and 4 cm^{-1} of band resolution, using a Thermo Scientific Nicolet iZ10 spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) equipped with a Smart Endurance™ (ZnSe crystal) apparatus. The samples were collected at room temperature, and the data were recorded using the OMNIC 9 software. The average spectra for the treated and washed cotton samples were normalised to the band at 1315 cm^{-1} (CH_2 wagging of cellulose), which falls in a region where the absorption bands of used chemicals are absent.

2.9 Colorimetric analysis

Colorimetric analysis was performed with a Datacolor Spectral Flash SF600X with the CIE (International Commission on Illumination) standard illuminant D65, at 10°. The CIE White Indexes were registered. Five measurements were taken for each sample, and the mean value was reported.

2.10 Mechanical properties

Mechanical properties (i.e., tensile strength and elongation at break) were carried out according to ISO 13934-1 using a Z005TH ProLine 5kN testing machine (ZwickRoell GmbH, Ulm, Germany) in the weft direction. Fabrics were cut into samples measuring 5 cm by 15 cm after being conditioned overnight at 20 ± 2 °C and 65 ± 5% RH. Elongation speed was set at 100 mm/min, and the distance between clamps was 10 cm.

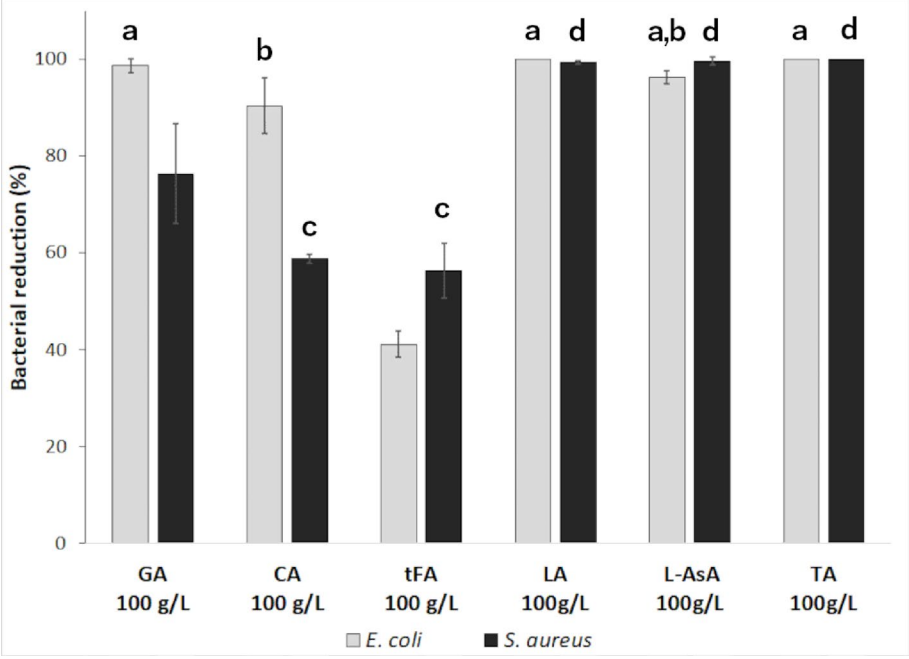

Fig. 4 Antibacterial reduction by the initial set of OAs (solution of 100 g/L) tested according to the ASTM 2149 – 2013 standard method with *E. coli* (grey) and *S. aureus* (black). Error bars represent standard deviation ($n = 3$). The same letters indicate not statistically significant differences among groups ($p < 0.05$, ANOVA followed by Tukey's post hoc test)

Table 4 Bacterial reduction rate of acid powders (liquid for LA) at 100 g/L

Active compound	Bacterial reduction %	
	S. aureus	*E. coli*
LA	99.4 ± 0.8	100
L-AsA	99.7 ± 0.4	96.3 ± 1.3
TA	100	100

3 Results and discussion

3.1 Preliminary test of the antibacterial action

The antibacterial tests were carried out on the initial set of selected OAs, i.e. CA, GA, tFA, LA, L-AsA, and TA, dissolved in deionised water at 100 g/L. The organisms selected for the tests were chosen as representatives for the Gram-positive (*S. aureus*) and negative (*E. coli*) classes.

A comparison of the bacterial reduction achieved by the six OAs is presented in Fig. 4 using histograms. For both bacteria, the bacterial reduction was 95% higher for LA, L-AsA, and TA (as shown in Table 4).

Based on the obtained results, CA and GA were excluded from further investigations, as they did not yield high bacterial reduction percentages against the tested bacteria (98.7% and 76.4% for gallic acid against *E. coli* and *S. aureus*, respectively, and 90.4% and 58.8% for caffeic acid against *E. coli* and *S. aureus*, respectively). Furthermore, the tFA was excluded due to the low bacterial reductions of 41.1% and 56.3% against *E. coli* and *S. aureus*, respectively.

3.2 Characterization of treated cotton fabrics

3.2.1 Analysis of surface morphology

Scanning electron microscopy was employed to determine whether the fabrics' morphology changes due to the deposition of proposed chemicals and the peculiar features of each analysed sample (Fig. 5a–d). Untreated samples showed grooves and natural twists typical of the surface morphology of unfinished fibres (Fig. 5a). However, after treatment, fibres were swollen, with clearly visible material on the surface, reflecting the presence of OAs in the form of consistent aggregates that reached 40 µm in size and presented an even distribution in the specimens (Fig. 5b). After the first wash with ECE detergent, the aggregates persisted, with reduced dimensions and density, and were detected only in the inner niches among the fibres (a white arrow indicates a tiny aggregate in Fig. 5c).

SEM micrographs revealed distinct differences in surface morphology between untreated and treated fabrics. The treated samples displayed a more continuous and uniform coating layer, with visible polymer deposition and fibre encapsulation. These surface features confirm the effectiveness of the finishing process in modifying the textile substrate and are consistent with the observed antimicrobial activity.

After being washed with ECE detergent, the samples treated with different combinations presented almost the same pattern as the unwashed references. The presence of the OAs in the unwashed sample was not distinguishable, and their loss was undetectable.

3.3 Contact angle

The wettability of the textiles, influenced by their geometric structure and chemical composition, was assessed through water contact angle (WCA) measurements. Due to the abundant hydroxyl groups in its structure, the high hydrophilicity of pristine cotton

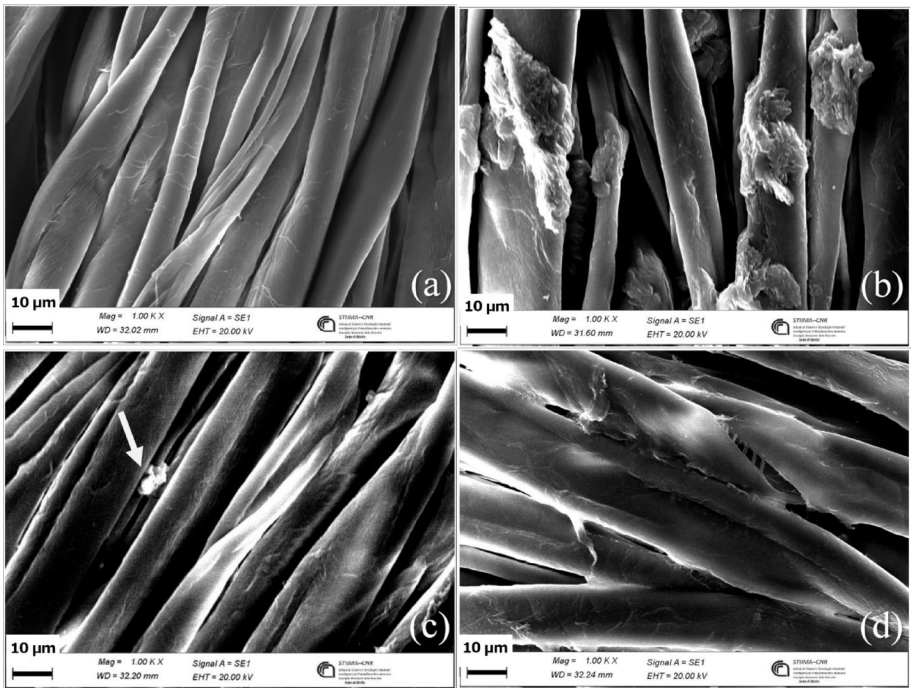

Fig. 5 Scanning electron microscopy images of the textile samples at 1000× resolution: (**a**) untreated cotton; (**b**) cotton impregnated with 10% TA; (**c**) cotton with 10% TA washed with ECE-98 type A; (**d**) cotton with PD biobased polymer binder containing 5% TA

causes an immediate absorption of water, making it impossible to measure the contact angle. The same type of response and relative absorption time (≤ 0.1 s) were observed for both the 10% and 5% OA-treated cotton samples, and this hydrophilic response could explain why the functionalisation was unable to withstand the washing simulations. In contrast, the treated samples exhibited a more pronounced hydrophobic nature, which can be attributed to the reduction of hydroxyl groups resulting from the presence of finishing treatments. The addition of the bio-based matrices led to an increase in absorption time and enabled the possibility to calculate the contact angle, which is presented in Table 5. The CA-based matrix presents features analogous to those of the cotton functionalised with the other three OAs, due to the similar chemical features. In contrast, for the Pluvion Dry biobased polymer binder, the absorption time could not be determined, as the biobased polymer binder functions as a waterproofing agent on fabrics.

3.4 FT-IR characterisation

The FT-IR analysis was performed to explore the presence of OAs and their durability on the cotton surface. In the FT-IR spectra, the absorption peaks of cellulose were observed in the profile of raw cotton at 3426 cm^{-1}, 2901 cm^{-1}, and 1113 cm^{-1}, corresponding to the stretching vibrations of O–H, C–H, and C–O–C, respectively. In the treated samples, the characteristic peaks of LA, L-AsA and TA are located at 1500–1800 cm^{-1} (which is around 1700 cm^{-1} for the stretching of C = O). These spectral modifications indicate successful functionalisation of cotton samples. As illustrated in Fig. 6, the characteristic peak of L-AsA is also located in the functionalised cotton spectrum, although with a lower signal; however, it becomes indistinguishable after the washing step with both the employed detergents. In contrast, when the treated fabric is dry-cleaned, the signal of the specific peak is lower but remains visible (Fig. 7). The described situation was observed for all the samples, and the Figs. 6 and 7 show only representative spectra.

3.5 Colorimetric analysis

The colorimetric analysis was performed on untreated cotton, fabrics treated with biobased polymer binders alone, and fabrics treated with 10% wt/vol of selected OAs in combination with biobased polymer binders.

The results show that the whiteness index of fabrics treated with biobased polymer binders alone remains close to that of untreated cotton, indicating minimal visual impact from the matrices themselves. In treatments with LA and TA across all biobased polymer binder types, the whiteness index remains relatively high, suggesting good aesthetic preservation. Conversely, L-AsA causes significant yellowing of the fabrics, especially

Table 5 Measurements of the contact angle and absorption time for the different matrices-treated cotton fabrics

Fabric	Contact Angle (°)	Absorption Time (s)
Citric acid (6%) cotton	–	0.1
Nearcoat BB-AC (10%) cotton	$117.7 \pm 2.6^{a,**}$	14.0
Vision Sugar 4.0 (10%) cotton	$124.2 \pm 7.5^{a,*}$	12.5
Pluvion Dry 2030 BS (10%) cotton	$138.4 \pm 2.1^{*,**}$	∞

ANOVA followed by Tukey's post hoc test:

[a] not statistically significant difference

$^{*}p < 0.05$

$^{**}p < 0.01$

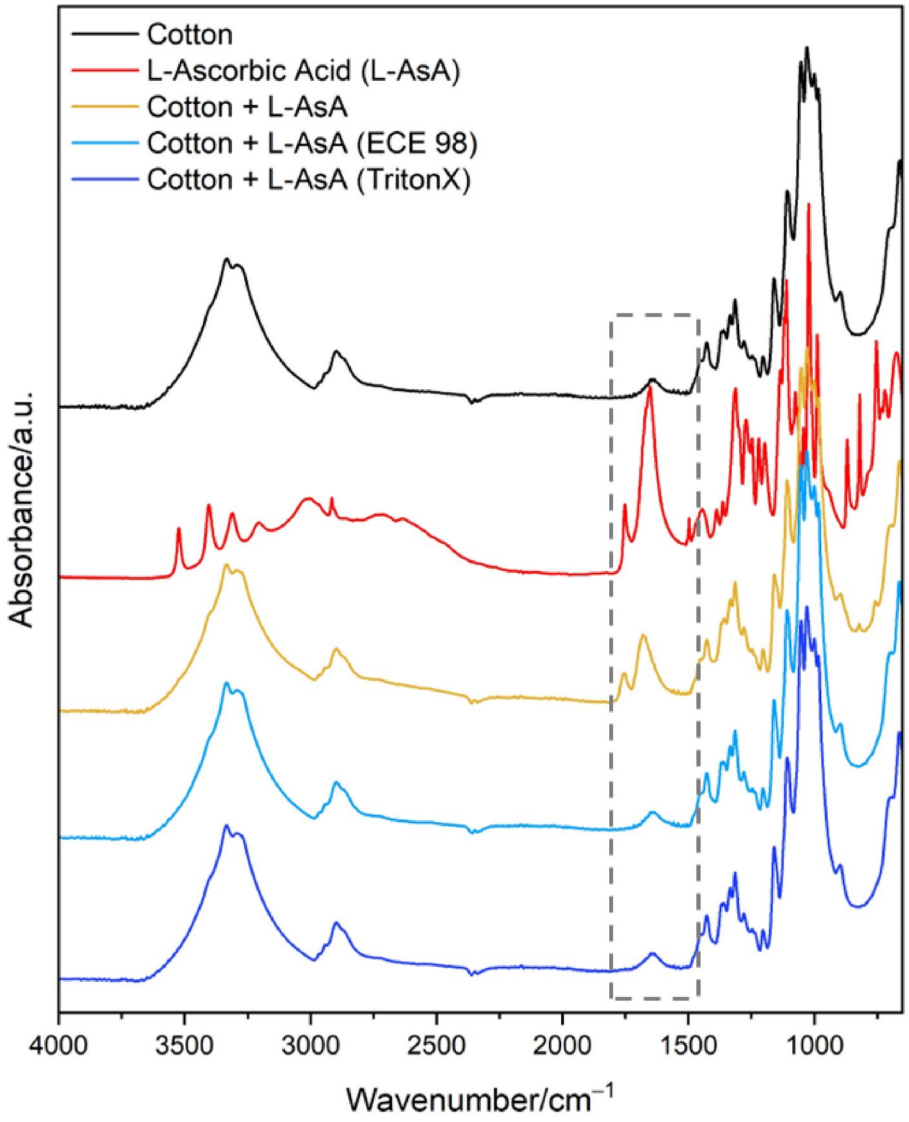

Fig. 6 FT-IR spectra of untreated cotton (black line), L-AsA powder (red line), 10% L-AsA-treated cotton (yellow line) and the corresponding washed samples (the two shades of blue). The area related to the stretching signals of the carboxylic groups is highlighted in the graph between the dashed lines (range 1500–1800 cm^{-1})

when combined with CitA. This yellowing effect can be attributed to the oxidative instability of L-AsA under the applied curing conditions (105 °C drying and 150 °C curing), leading to its decomposition and the formation of brownish oxidation products, such as dehydroascorbic acid and further polymerized derivatives. These oxidized species absorb in the visible spectrum and are responsible for the marked decrease in the whiteness index. This phenomenon is particularly exacerbated in the presence of CitA, possibly due to enhanced catalytic effects on the degradation process in acidic environments (Table 6).

3.5.1 Mechanical properties

The mechanical properties of pristine cotton and samples treated with biobased polymer binders, as well as those treated with biobased polymer binders combined with 10% wt/vol of selected OAs, were evaluated.

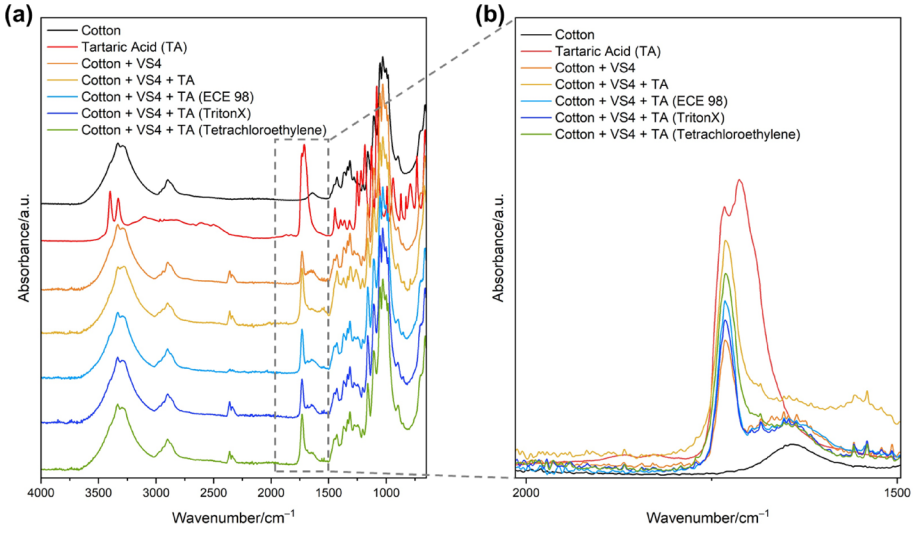

Fig. 7 **(a)** FT-IR spectra of untreated cotton (black line), TA powder (red line), 10% VS4 and 5% TA biobased polymer binder-treated cotton (orange and yellow line respectively), the corresponding washed samples (the two shades of blue) and the dry-cleaned sample (green line). **(b)** Zoom of the area of interest, which lies between 1500 cm^{-1} and 1800 cm^{-1}, where the characteristic peaks of the OAs are located; these disappear after washing, except for the sample treated with tetrachloroethylene

Table 6 CIE white indexes of treated samples

Sample	CIE White Index
Untreated cotton	73.58
CitA	69.55
CitA/LA	69.51
CitA/L-AsA	-83.53
CitA/TA	67.00
VS4	74.33
VS4/LA	63.79
VS4/L-AsA	-26.14
VS4/TA	51.47
Nbbac	74.58
Nbbac/LA	57.04
Nbbac/L-AsA	-23.57
Nbbac/TA	47.89
PD	72.29
PD/LA	58.00
PD/L-AsA	-25.04
PD/TA	51.80

The untreated cotton fabric exhibited a tensile strength of 410 ± 9 N and an elongation at break of 25.9 ± 0.5%. All finishing treatments resulted in a reduction in mechanical performance compared to the untreated fabric. Treatments using biobased polymer binders alone induced only a slight decrease in tensile strength and elongation, suggesting a limited impact of the bio-based matrices on the integrity of the cotton fibres.

In contrast, treatments involving TA significantly compromised the mechanical properties, resulting in a substantial reduction in tensile strength and elongation, except when TA was combined with CitA, in which case the mechanical properties were better preserved.

This mechanical deterioration can be attributed to the multiple hydroxyl and carboxyl groups of TA, which may promote partial hydrolysis of glycosidic linkages of cellulose during the curing process. Such chemical interactions can weaken the cotton fibre structure. On the other hand, the combination of TA with CitA likely stabilises the system through esterification reactions with cellulose under curing conditions, thereby partially preserving the fibre's mechanical integrity. Other combinations involving LA and L-AsA with various matrices showed moderate reductions in strength but maintained acceptable mechanical properties, indicating a less aggressive interaction with the cellulose structure under the employed processing conditions (Fig. 8).

3.6 Antibacterial properties of unwashed fabrics

The cotton samples were treated with LA, L-AsA and TA to verify the efficacy of these OAs as antibacterial agents for cellulose-based fabrics using the dip-coating technique, and the concentration of the OA solutions was 10% wt/vol. The treated fabrics were tested against *E. coli* and *S. aureus* according to the ASTM 2149 – 2013 standard. The bacterial reduction rate was higher than 95% for all the samples, as presented in Table 7.

3.7 Antibacterial properties after laundering

The durability of the produced functionalised cotton samples in relation to washing cycles was evaluated by the modified standard ISO 105-C06, which is a procedure for testing colour fastness against simulated domestic and industrial laundering. Two different washing surfactants, ECE detergent (ionic) and Triton™ X-305 (non-ionic), were utilized for this test. It was found that, regardless of which surfactant was used, the functionalisation did not last after laundering.

This phenomenon can be explained as a leaching or release of the active compounds due to the washing conditions. The washed samples were tested against *E. coli*, which revealed a partial or complete loss of antibacterial ability, as represented in Fig. 9. This was probably due to the lack of crosslinks between the cotton fibre and the acid. Considering this evidence, the antibacterial tests against *S. aureus* were not performed.

The observed loss of antibacterial activity after washing cycles can be attributed to the partial removal of the coating or hydrolytic degradation of the chemicals. The interactions between finish agents and cellulose chains are mainly the result of hydrogen bonds and esterification, which lack the chemical stability required to resist repeated laundering. Indeed, hydrogen bonds can be easily disrupted by water and surfactants, while ester bonds are susceptible to hydrolysis in aqueous environments, particularly in the presence of detergents and elevated temperatures, which can accelerate their cleavage and lead to leaching of the functional agents. Additionally, molecular characteristics of the acids may influence their retention; TA, for instance, showed better post-wash performance, likely due to a higher number of functional groups and stronger affinity for both the fibre and the binder matrix. These insights provide a useful basis for future optimisation of OA-based coatings regarding durability and formulation stability.

3.8 Optimization of OAs concentration for cotton treatment

In parallel, the employed concentration for each OA was halved to 5% (w/v) to optimise the process to better align with market demands. The tests conducted on the samples impregnated with the OAs at half the concentration revealed that the samples' efficiency

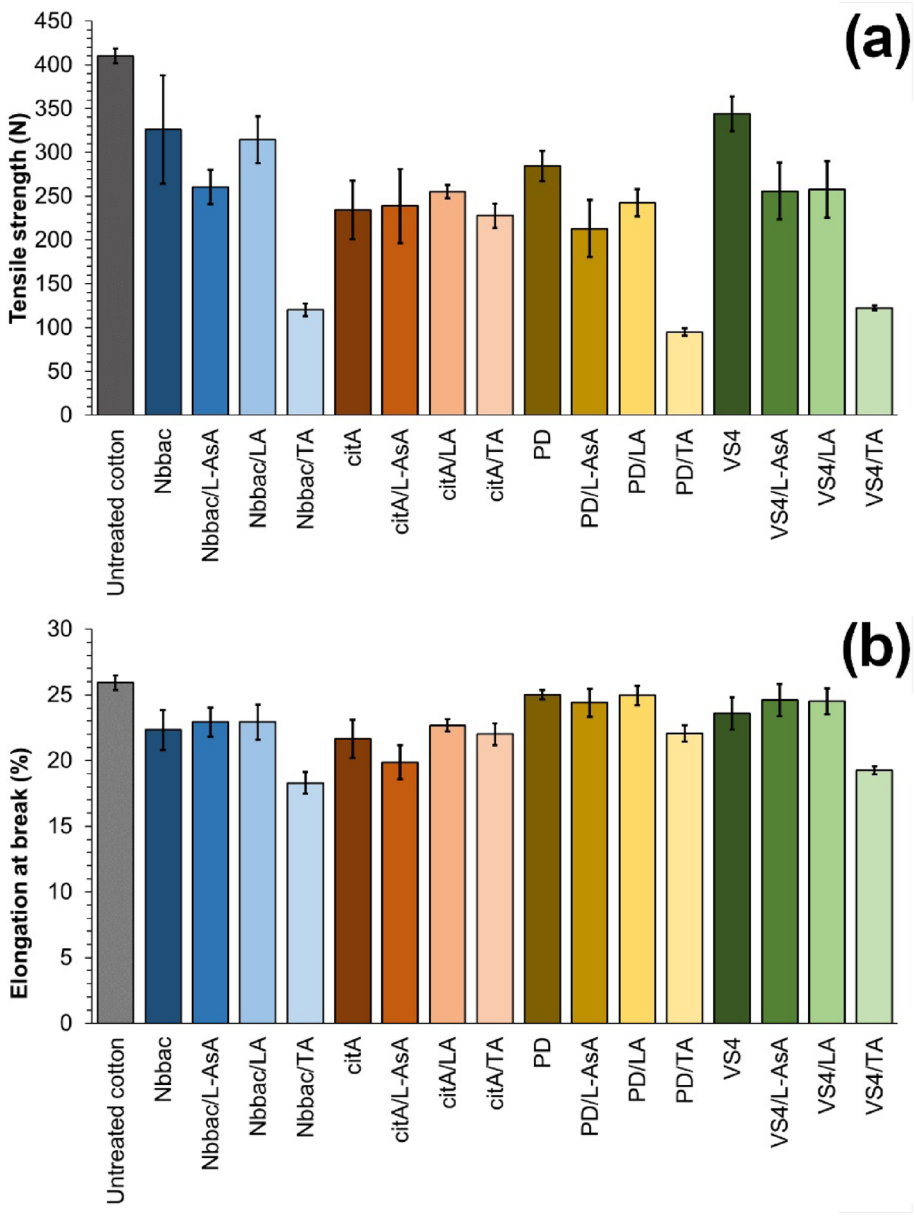

Fig. 8 Mechanical properties of treated and untreated fabrics: (**a**) Tensile strength; (**b**) Elongation at break

Table 7 Bacterial reduction rate for treated cotton at a 10% wt/vol concentration

Fabric	Treatment	Bacterial reduction %	
		S. aureus	***E. coli***
Cotton	untreated	0	0
	LA	98.7 ± 1.8 [a]	100 [b]
	L-AsA	99.0 ± 0.2 [a]	95.5 ± 0.1 [c]
	TA	100 [a]	99.5 ± 0.7 [b, c]

[a,b,c] not statistically significant difference (ANOVA followed by Tukey's post hoc test)

was higher than 85%, which was then chosen as a threshold. The results are presented in detail in Table 8 and compared to the previous results in Fig. 10.

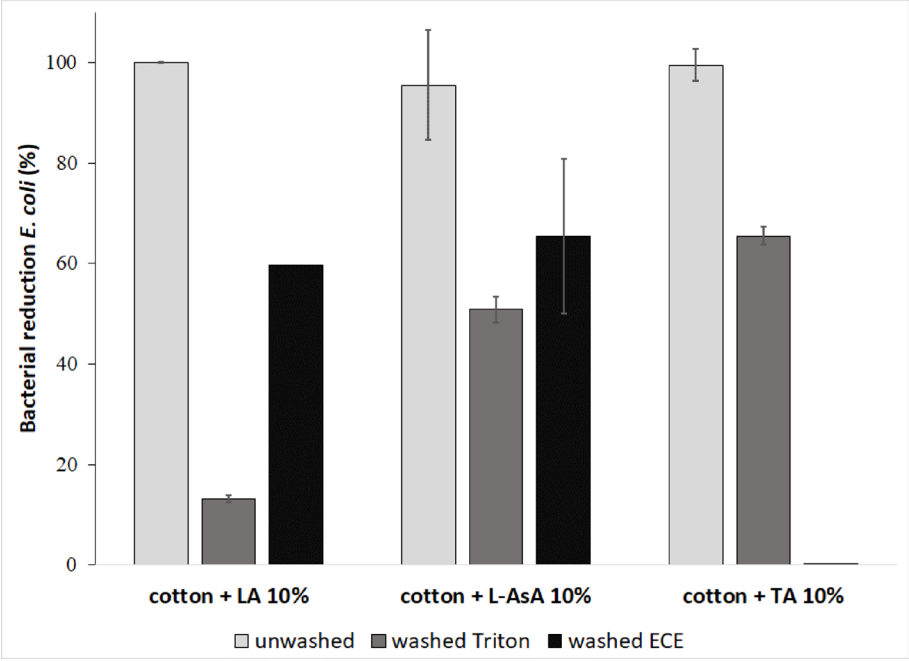

Fig. 9 Antibacterial ability of the treated cotton after washing with Triton X-305 (grey), ECE detergent (black) and unwashed (light grey), tested against *E. coli* according to the ASTM 2149 – 2013 standard

Table 8 Bacterial reduction rate of treated cotton at a 5% wt/vol concentration

Textile fabric	Treatment	Bacterial reduction %	
		S. aureus	*E. coli*
Cotton	LA	99.3 ± 0.3 [a]	99.8 ± 0.3 [b]
	L-AsA	90.0 ± 4.7	85.0 ± 3.4
	TA	100 [a]	96.4 ± 0.4 [b]

[a, b] not statistically significant difference (ANOVA followed by Tukey's post hoc test)

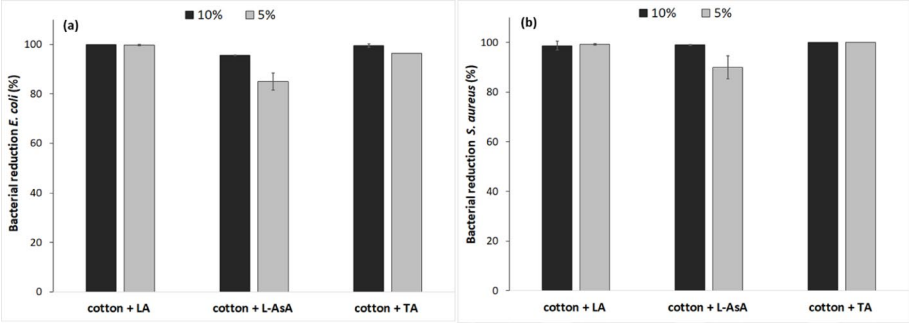

Fig. 10 Comparison of antibacterial reduction of the cotton samples treated with OAs with 10% and 5% (w/v) concentrations against (a) *E. coli* and (b) *S. aureus*

3.9 Combination of OAs and bio-based matrices

The half OA concentration was retained, and the focus was brought back to washing fastness. LA, TA, and AA were individually coupled with four different commercial bio-based polymer binders, which ranged from 39% to 56% bio-based ingredients. The solutions were then used to impregnate cotton samples using the foulard technique, which were tested against *S. aureus* and *E. coli*. Next, the solutions that yielded a higher than

Table 9 Bacterial reduction rate for cotton treated with the combinations of OAs (5%) and cita (6%)

Fabric	Treatment	Bacterial reduction %	
		S. aureus	***E. coli***
Cotton	CitA	80.3 ± 2.1 [a]	11.6 ± 5.2
	CitA/LA	83.6 ± 1.2 [a]	42.8 ± 2.1 [b]
	CitA/L-AsA	81.9 ± 1.4 [a]	42.8 ± 7.7 [b]
	CitA/TA	92.5 ± 0.8	70.7 ± 4.9

[a, b] not statistically significant difference (ANOVA followed by Tukey's post hoc test)

Table 10 Bacterial reduction rate for cotton treated with the combinations of OAs (5%) and VS4 (10%)

Fabric	Treatment	Bacterial reduction %	
		S. aureus	***E. coli***
Cotton	VS4	0	0
	VS4/LA	79.8 ± 7.9 [a]	99.0 ± 1.4 [b]
	VS4/L-AsA	85.7 ± 4.4 [a]	69.6 ± 2.0
	VS4/TA	100	100 [b]

[a, b] not statistically significant difference (ANOVA followed by Tukey's post hoc test)

Table 11 Bacterial reduction rate for cotton treated with combinations of OAs (5%) and Nbbac (10%)

Fabric	Treatment	Bacterial reduction %	
		S. aureus	***E. coli***
Cotton	Nbbac	0	0
	Nbbac/LA	75.0 ± 1.3	98.2 ± 0.6 [a]
	Nbbac/L-AsA	90.0 ± 2.1	75.6 ± 3.1
	Nbbac/TA	100	100 [a]

[a] not statistically significant difference (ANOVA followed by Tukey's post hoc test)

Table 12 Bacterial reduction rate for cotton treated with combinations of OAs (5%) and PD (10%)

Fabric	Treatment	Bacterial reduction %	
		S. aureus	***E. coli***
Cotton	PD	0	0
	PD/LA	99.2 ± 0.2 [a]	99.1 ± 1.3 [b]
	PD/L-AsA	97.0 ± 0.8	93.4 ± 1.9
	PD/TA	99.4 ± 0.4 [a]	100 [b]

[a, b] not statistically significant difference (ANOVA followed by Tukey's post hoc test)

85% bacterial reduction were selected for the laundering procedures. The combinations and the relative bacterial reduction rates are listed in Tables 9, 9, 11 and 12. CitA was the only matrix to present an antibacterial effect per se (as reported in Table 9), while the bacterial reduction for the other three biobased polymer binders when ed with cotton without the OAs was 0%. This can be attributed to the fact that CitA is an OA itself, known for its antimicrobial properties [10]; however, it did not show any synergistic effect when combined with the selected acids. This may be related to the composition of the solution employed or a hypothetical interaction with the other OAs, resulting in the sequestration of the functional groups involved in the mechanism. Moreover, CitA exhibits a relative selectivity in its antibacterial effect against *S. aureus*. The samples treated with the CitA-OAs couples were subsequently excluded from further laundering tests, as well as the other combinations that provided a bacterial reduction rate of

Table 13 Bacterial reduction rates of cotton treated with LA (5%) and the selected combinations of LA and biobased polymer binders after dry-cleaning simulations. The cells for the other combinations have been left empty

Fabric	Treatment	Bacterial reduction %	
		S. aureus	*E. coli*
Cotton	LA	81.8 ± 0.3	100
	VS4/LA	-	64.5 ± 10.5 [a, b]
	Nbbac/LA	-	56.9 ± 3.4 [a]
	PD/LA	88.6 ± 3.7	78.1 ± 4.6 [b]

[a, b] not statistically significant difference (ANOVA followed by Tukey's post hoc test)

Table 14 Bacterial reduction rates of cotton treated with L-AsA (5%) and the selected combinations of L-AsA and biobased polymer binders after dry-cleaning simulations. The cells for the other combinations have been left empty

Fabric	Treatment	Bacterial reduction %	
		S. aureus	*E. coli*
Cotton	L-AsA	67.5 ± 0.1	93.8 ± 1.9
	VS4/L-AsA	81.1 ± 0.3	-
	Nbbac/L-AsA	64.6 ± 0.9	67.5 ± 0.3
	PD/L-AsA	92.6 ± 1.0	79.7 ± 0.1

Table 15 Bacterial reduction rates of cotton treated with TA (5%) and the selected combinations of TA and biobased polymer binders after dry-cleaning simulations

Fabric	Treatment	Bacterial reduction %	
		S. aureus	*E. coli*
Cotton	TA	100 [a]	100 [c]
	VS4/TA	98.8 ± 0.1 [b]	100 [c]
	Nbbac/TA	99.7 ± 0.5 [a, b]	99.2 ± 0.1 [c]
	PD/TA	99.7 ± 0.5 [a, b]	97.2 ± 2.9 [c]

[a, b,c] not statistically significant difference (ANOVA followed by Tukey's post hoc test)

less than 85% against *E. coli*. The combinations that showed higher antibacterial activity (up to 100%), as described in Tables 9, 11 and 12, highlight the performance of TA, in particular.

The laundering fastness tests were performed against *E. coli* to determine whether the coupled OAs and matrices help overcome the limitations associated with washability. The selected combinations (VS4/LA, VS4/TA, Nbbac/LA, Nbbac/TA, PD/LA, PD/L-AsA, and PD/TA) presented bacterial reduction rates ranging from 0% to 63.9%, with the high variability being attributed to random phenomena of leaching that occur during the washing process.

3.10 Antibacterial properties after dry-cleaning

The evidence demonstrating the loss of the antibacterial compound after the first wash led to an attempt to carry out a dry-cleaning simulation using tetrachloroethylene. The bacterial reduction evaluations were performed for both *S. aureus* and *E. coli* for cotton samples treated with the OAs and with combinations of the OAs and biobased polymer binders. The results, presented in Tables 13, 14 and 15, confirm the hypothesis of leaching occurring during the washing step. Washing with a solvent instead was milder and resulted in better washing fastness, which is quite significant, particularly for TA and the associated combinations. It should be noted that the presence of the matrices does not

boost antibacterial fastness for the fabrics, which exhibit the same resistance to washing regardless of the addition of the matrices. The persistence of OA, which is responsible for the antibacterial activity, is visible in Fig. 7 as the typical FT-IR peak of the carboxylic group, even if partially reduced, after the dry-cleaning.

4 Conclusions

This work demonstrated the potential of selected OAs as sustainable antibacterial finishing agents for cotton fabrics, applied either individually or in combination with bio-based polymeric and polycarboxylic binders. The study confirmed that several OAs exhibit notable antibacterial efficacy against both Gram-positive and Gram-negative bacteria, highlighting their suitability as natural alternatives to conventional antimicrobial agents. The incorporation of bio-based biobased polymer binders improved the fixation of OAs onto the cotton substrate, leading to enhanced wash durability and reduced loss of antibacterial performance after laundering.

Among the tested systems, specific OA–biobased polymer binder combinations achieved high bacterial reduction while maintaining acceptable mechanical integrity and fabric handle. Microscopic and spectroscopic analyses revealed that hydrogen bonding and partial esterification between hydroxyl and carboxylic groups contributed to the formation of a coating on the cotton surface. These interactions are key to understanding the durability and efficiency of the developed functional finishes.

Overall, the findings support the feasibility of using water-based, bio-derived formulations to produce antimicrobial textiles with enhanced environmental compatibility. This approach aligns with the growing demand for non-toxic, formaldehyde-free, and renewable finishing strategies in the textile industry.

In contrast to prior formulations relying on free acids or synthetic binders, the combination with biopolymers such as polyacrylate derivatives (e.g., Nearcoat BB-AC, Vision Sugar 4.0 and Pluvion Dry 2030 BS) demonstrated not only high initial antimicrobial efficacy but also improved retention of performance after dry-cleaning procedures.

The use of tartaric acid, in particular, in conjunction with biopolymeric carriers, showed the most promising results in terms of efficacy and retention post-cleaning, suggesting a viable pathway for the development of antibacterial textiles suited for healthcare, hygiene, and packaging applications. This expands the applicability of bio-based coatings beyond disposable or single-use formats, representing a significant innovation over existing OA-only or biobased polymer binder-only strategies.

This research paves the way for the design and development of innovative, dry-cleaning-resistant, bio-based coatings for cotton fabrics that are durable and efficient in terms of antibacterial properties. However, some issues still need to be addressed, such as poor water washing durability, cotton yellowing, and reduced mechanical properties. Currently, these materials could potentially find applications as disposable and single-use textiles, which can be employed, for instance, in the medical, biomedical, and packaging industries. Future work could also assess the biocompatibility of the proposed finishing formulations.

Author contributions

V. Basile : Writing – original draft. M. Piccioni : Investigation. A. Varesano : Writing – review and editing. M.R. Plutino : Writing – review and editing; Supervision. G. Rando : Investigation. G. Rosace : Writing – review and editing; Supervision. V. Trovato : Investigation. C. Vineis : Writing – review and editing; Supervision; Project administration.

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Data availability
All data supporting the findings of this study are available within the article.

Declarations

Ethics approval and consent to participate
Not applicable.

Consent for publication
Not applicable.

Competing interests
The authors declare no competing interests.

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