Original article

A preliminary evaluation of chemical interaction between sanitizing products and silk

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Abstract

The ongoing Coronavirus crisis involved almost all sectors as well as museums, collections, and historical sites all over the world. Even though artworks do not have the ability to spread the virus, the pandemic officially introduced in cultural sites alcohol-based products (even by visitors for personal use) as these products were indicated to be able to inactivate the virus and were imposed by many local authorities. In this context, the need to conciliate the safety of the visitors and the protection of artworks represents a challenging task. The possibility that accumulation of vapour coming from the sanitizing solutions or from accidental spills, potentially caused also by visitors, should be considered.The study focuses specifically on the possible interactions between sanitizing alcohol-based products and silk, since this material is present in many cultural sites all over the world on upholsteries and tapestries. The recommended sanitising solution (75% ethanol, 20% water, 5% benzalkonium chloride) selected by the Italian Ministry for Cultural Heritage (MIBACT) was considered. Pure distilled water, absolute ethanol and water/ethanol blends in different concentrations were also tested. Chemical and morphological variations on the silk have been evaluated with Scanning Electron Microscopy - SEM, Atomic Force Microscopy - AFM and portable instruments (contact microscope, colorimeter, Infrared and Raman spectroscopy). IR and Raman analyses did not detect significant chemical changes in silk. However, Raman spectra showed, after immersion treatments, minor variations in the intensity of peaks attributed to dyes. Residues of benzalkonium chloride after immersion tests in sanitising solution are present, confirmed also by SEM and AFM analyses. Even if chemical spectroscopic changes were not relevant, the colour of few samples seemed to consistently fade after immersion treatments, thus affecting the visual appearance of textiles.

Keywords:

Silk preservation, Sanitisation, Chemical and morphological evaluation

1 Introduction

Since the end of 2019, the world has been involved in a pandemic due to the rapid spread of a new virus of the coronavirus family, also known as Covid-19.

The global Coronavirus crisis has had and will have an unprecedented impact on museums and historical sites all over the world [1].

Conservators, researchers and stakeholders have been monitoring and studying the situation, reflecting on the status quo and on what might come next. The attention to this situation is testified by some international projects, devoted to

understand for how long the virus can survive on the surface of art objects, depending on the materials, and analysing the economic and social impact of the pandemic on museums [2,3]. Many museums, despite being considered as safe places, thanks to enforced social distancing, limited or controlled number of visitors and hygiene measures (such as FFP2 masks and hand sanitizers) are still closed [4].

The use in museums of sanitising solutions for personal hygiene and general use is now widely employed and recommended. Sanitising practice aims at inactivating Covid-19 virus, but it may have drawbacks depending on the places where it is performed. Beside the health risk management for visitors, there is a general concern for estimating and understanding possible risks related to sanitising protocols for artworks and objects, as pointed out also in Italy by the Higher Institute for Conservation and Restoration (ISCR), (Istituto Superiore per la Conservazione e il Restauro - ISCR) [5–7]. The necessity to conciliate the safety of the visitors and the protection of artworks represents, therefore, a challenging task.

Due to the pandemic, most of the latest researches have been focused on evaluating the efficiency of sanitizers and their components against Covid-19 [8–12]. Several products were reported to successfully inactivate Covid-19 virus, such as ethanol (70–90%), chlorine-based products, and hydrogen peroxide. Next to these, the application of ozone and UV rays is also effective for the disinfection process, but not all these methodologies are compatible with artworks [1,5,6,13]. Italian Ministry for Cultural Heritage (Ministero per i beni e le attività culturali e per il turismo -MIBACT) recommended using solutions mainly composed of ethanol and water blends, avoiding chlorine-based products, as well as O_3, H_2O_2 and UV rays, due to their riskiness for the conservation of many heritage materials [5–7]. Despite the fact that alcohol-based solutions (with a concentration at least above the 70%) seem to be effective to inactivate the virus [11], the MIBACT indicates also the addition of benzalkonium chloride (BZK) to the ethanol/water blends, due to its antimicrobic and ionic action that reduces the material surface tension, facilitating the contact of solutions [6].

Alkyldimethylbenzylammonium chloride, also known as benzalkonium chloride (BZK), is a well-known low-cost antibacterial commonly used for commercial, domestic, and medical applications. It is also present in various disinfectant and finds a frequent application in the food industry. BZK is an ionic liquid and usually do not cause skin irritation. The antibacterial action is usually linked to its ability to alter the cell membrane permeability, which loses its coherence. BZK is able to inactivate many viruses and also bacteria [9,10,14]; its efficiency can vary based on temperature, concentration and, of course, time of exposure. Up to now, recent literature has not evidenced a direct correlation between antibacterial and antiviral performances of sanitising products, showing also that BZK does not seem to positively improve the products' antiviral action [11]. Most of the studies highlighted the need to further validate the efficacy of sanitizers in general and to release strict guidance regarding their production [11,12].

So far, no specific systematic studies have been conducted on the possible effects and impacts on art materials of frequent sanitisations [13]. Among Cultural Heritage materials, silk is of great interest in evaluating the possible effects and impacts of cleaning and sanitising products, due to its diffusion, historical relevance, and fragility [15]. In fact, silk is commonly present in historic museums, places of worship, and historic houses all over the world (tapestries, upholsteries, clothes, etc.).

Silk possesses many unique properties that made it an appealing material, known since the 3rd millennium BCE [16], it is characterized by high tensile strength and can be dyed in a wide range of shades [17,18].

Silk is a biopolymer composed of two proteinaceous structures made by two fibroin filaments (around 66%wt) coated with sericin (around 26wt%). Sericin, however, gets often removed during thread production treatments, leaving fibroin as the only component of many silk textiles [19]. The use of un-degummed (raw) silk is in some case, however, preferred due to the peculiar texture, strength, and generally higher affinity for dyes [19–22].

Fibroin's primary structure consists of a series of 18 amino acids (e.g. glycine (44.6%), alanine (29.4%), serine (12.1%), tyrosine (5.1%), phenylalanine (0.4%), and tryptophan (0.1%)). Secondary structure, instead, is characterised by the so-called β-sheet conformation which is surrounded by amorphous regions [15,19]. Silk can be described as a semi-crystalline material where crystalline regions (responsible for silk characteristic strength) are surrounded by amorphous portions (that give the fibre resilience), made up mainly of tyrosine residues [18,19,22,23].

Despite its remarkable characteristics such as strength and lustre, silk is subject to several degradation processes, such as hydrolysis, oxidation, as well as damages correlated to light, heat, or mechanical stresses [15,18,19,22,24,25]. When necessary, silk is subjected to cleaning, by wet and dry procedures, depending on the conservation state of the fabric, on the nature of the dirt to be removed and on the presence of previous restoration interventions [20]. Wet cleaning, in particular, is widely used for the conservation of historical textile and it can be done using mainly water alone or mixed in different proportion with solvents, buffers, chemicals and specific agents (such as sequestering agents, bleaching agents and enzymes) [22,26,27].

Among organic solvents, alcohol is mainly employed in wet solvent cleaning methods and in adhesives treatments or removals [22,27–29]. Alcohol can easily penetrate textiles even without surfactants, as it helps reducing the surface tension of the material [22,26]. In particular, alcohol can be sprayed on an area treated with water; its faster drying rate

would help to prevent the formation of swill mark. Alcohol can also be mixed with water to relax degraded fibres where water alone, due to its high surface tension, may cause damages [22,26]. Time of contact and concentration need, of course, to be cautiously evaluated as solvents such as alcohols and ketones can cause desiccation of textile due to the extraction of bound water from the fibres [22,26]. Alcohols are also able to affect protein folding, desolvating peptide amide groups by acting as hydrogen bond donors, therefore altering local protein structure [30]. Additionally, the stability of dyes and possible colour changes should be evaluated before the application for cleaning purposes [18, 22,26].

Research aim

This research was borne in June 2020, when museums and churches reopened after the first Italian Covid-19 lockdown. The aim was to investigate possible impacts of ethanol-based sanitising solutions on silk, as extensively present in historic buildings, e.g. as wall decoration.

Although artworks do not spread virus, as visitors are not supposed to touch them, the necessity to apply new cleaning protocols and products was of concern. Accidental spill of sanitizers, potentially caused also by visitors and accumulation of vapors due to ordinary sanitisation could damage artefacts, such as textile decorations. For evaluating silk sensitivity to sanitizing products, we propose a multi analytical approach, based on morphological observations, colorimetric analyses, spectroscopic analyses (FTIR and Raman). Scanning Electron Microscopy and Atomic Force Microscopy where also applied to selected samples, to better evaluate possible visible modifications of silk after contact with sanitizing products.

2 Materials and methods

2.1 Silk samples

The effects of ethanol-based sanitising solutions on historical silks were evaluated on four silk fabrics showed in Fig. 1.

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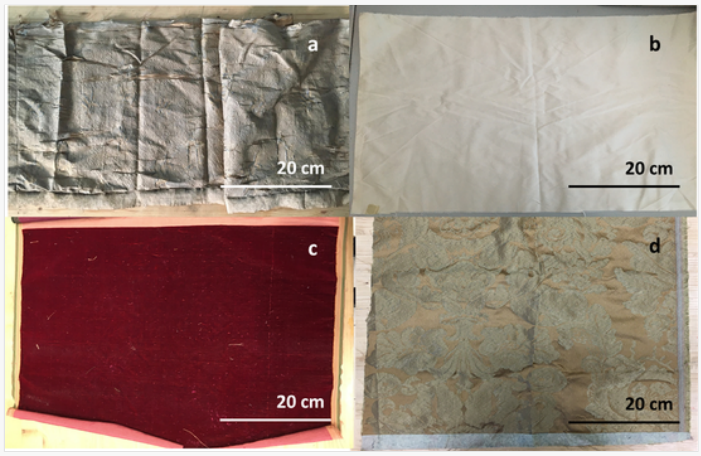
Fig. 1



silk samples. a) Greenish silk produced most likely in the past century, used as tapestry in the Fondazione Querini Stampalia Museum - Venice; b) White contemporary industrial silk; c) Red contemporary velvet produced with traditional methods (Bevilacqua La Masa - Venice); d) Yellow contemporary silk produced with traditional methods (Bevilacqua La Masa - Venice).

The silk (a) was kindly provided by the Querini Stampalia Museum in Venice. The age of the textile is unknown, and it was stored in the Museum deposit without any indication, belonging probably to a previous museum wall textile. The fabric is realized joining two different threads, one yellow and the other green/gray. The silk fabrics was probably realised using mainly degummed silk characterised by independent single smooth and structureless filaments. Next to the most common Bombyx mori silk threads, the presence of wild silk (i.e. Tussah – see Supplementary Materials – Appendix 1A), unevenly thick and band shaped with fine vertical stripes, cannot be excluded [18,31]. It has a mass density of 0,012 g/cm^2 and a thread density of 40 threads/cm in each direction. The number of warp and weft threads per unit length of each silk fabric was determined by counting the threads per length of 1 cm in the warp and weft direction. The fabric is characterized by a floral pattern that is still visible despite being the material in a bad conservation state. Many threads separated from the edges, loss parts, weakened fibers, and brittleness combined with staining and dust are clearly visible. At the edges, some metal nails were found indicating its use, probably, as wall decoration. No specific procedure was performed to remove dust (apart from gentle shaking), since the material was quite fragile.

The sample (b) is a white plain silk purchased in 2019 in a manufacture in Venice specialised in fabrics for tapestries. According to the seller, the fabric was made with an industrial loom probably using degummed and bleached silk (no specifications on the two processes were available). The fabric has a thread density of 50 threads/cm in each direction and a mass density of 0,007 g/cm^2.

The red silk velvet (c) was donated by Bevilacqua, an artisan factory in Venice, and was in good conservation state with no evidence of defibering or brittleness. The textile was part of a larger production made in the last decade for the renovation of the interior decoration of a Museum in Germany. According to the producers, the tools and techniques employed were still the traditional ones performed in XVIII century [32]. The red silk velvet has a mass density of 0,037 g/cm^2 and its weft has a density of 10 threads/cm.

The last investigated fabric (d) is a yellow silk also produced in the last years by Bevilacqua factory, with a mass density of 0,013 g/cm^2 and a thread density of 30 threads/cm for the weft and 40 threads/cm for the warp. Original XVIII looms and traditional techniques (such as tricks of weaving the cloth using some damp threads for decorative purposes) were employed in this case too. This fabric, like the Querini one, presents a decorative floral pattern and three yarns different for colour and aspect were distinguished (see Supplementary Materials – Appendix 1A). Specifically, a yellow thread was used for the weft while two different yarns were used for the warp: a yellow and a gray one. The gray yarn may be identified, most probably, as cotton due to the characteristic twists and distortions [18, 31].

No specific information regarding the dyeing process was given for the red and the yellow silks.

To obtain similar samples, easy to manipulate and test, the fabrics were cut into rectangular pieces measuring 5 cm width x 8 cm length. Red silk velvet samples, due to the peculiar fabric weaving, were sewed at sides, to prevent defibering. When cut, the red silk velvet tended, in fact, to roll up and this would for sure have affected the tests, as the surface would not have been exposed to the treatment in the same way. Plastic sticks were sewed diagonally at the back of each sample fixing them only on the edges of the fabric, leaving the rest of the samples free.

No preliminary dye bleeding tests were performed before the experiments with the different products not to affect the selection of the fabrics.

2.2 Sanitising agents

The sanitising solution, here employed, was prepared in the laboratory following the MIBACT – Soprintendenza di Roma indications [6]. The solution was obtained mixing 50 ml of benzalkonium chloride - BZK (50% in water - purchased from Antares s.r.l. Bologna) with 200 ml deionized water and 750 ml ethanol (ultrapure, VWR Chemicals).

Pure ethanol, deionized water, and solutions of ethanol/water in different concentrations (50%, 70%, 75%, and 79%) were also tested for evaluating the possible effects or impacts caused by each blend component. The impact of BZK on silk fabrics was evaluated by comparing the results versus ethanol/water blends. The four ethanol concentrations were chosen to be representative of commercially available sanitisers. These, in fact, usually have a concentration of alcohol between 60% and 90% [8,11].

2.3 Treatment of silk samples

Museums and collections are safe places for artworks conservation; objects are, when possible, stored in showcases, the microclimate is monitored and security guards the behaviour of visitors. This may be different or more complicated in the case of historic buildings or churches when economic limits are present, or improvements cannot be done due to building conservation policies. Even though artefacts are not supposed to be touched by visitors and do not have the ability to spread virus, the possibility that visitors may damage, for examples a wall tapestry or furniture, cannot be excluded.

According to the research aim, the samples' treatments simulate two possible way of contact between silk and sanitizing in liquid or vapour state.

Specifically:

i) 10 days exposure to sanitising solution vapours;

ii) immersion in sanitising solutions.

Scenario i) was simulated exposing silk samples to sanitising solution vapours for 10 days in a closed environment, thinking of repeated sanitisation of a closed room. For this, a glass desiccator of a total volume of 3 l was filled with 250 ml of sanitising solution, temperature and relative humidity in the desiccator were monitored during the experimentation with a datalogger (T=25°C±2; RH=65%±5). The samples were hanged within the desiccator using a nylon strand positioned at a distance of 15 cm from the solution.

Scenario ii) was done immersing the silk samples for 30 minutes (short contact) and 24 hours (prolonged contact) in MIBACT sanitising solution, water, ethanol, and ethanol/water blends at different concentrations. The two immersion tests were selected to exacerbate the contact and to understand if the use of sanitising products would represent a real conservation risk for silk. After immersion, the product was intentionally not rinsed with water, letting the products to dry naturally. If accidental contact between silk and sanitisers may occur, spills might not be noticed and therefore not rinsed or removed.

Table 1 summarises the different treatments performed.

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Table 1

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treatments performed on silk samples.

Treatment	Type of treatment	Solution used	Treatment duration
t1	Vapour exposure	MIBACT sanitising solution	10 days
t2	Immersion	MIBACT sanitising solution	30 minutes
t3	Immersion	MIBACT sanitising solution	24 hours
t4	Immersion	Deionized Water	24 hours
t5	Immersion	Ethanol Absolute	24 hours
t6	Immersion	Ethanol 50%	24 hours
t7	Immersion	Ethanol 70%	24 hours
t8	Immersion	Ethanol 75%	24 hours
t9	Immersion	Ethanol 79%	24 hours

After treatments, all samples were stored in the laboratory (T=25°C±2; RH=65%±5) into open glass containers for at least one week before running chemical and morphological analyses, as described in the next paragraphs.

2.3 Analytical methods

2.3.1 Morphological characterisation

Morphological observations of samples were performed using a portable contact microscope (Dino Lite Premier AM4113/AD4112 series). All samples were analysed both under VIS and UV light at two different magnifications (50x and 220x). The identification of the threads present in the silk fabrics were done at 40x magnification using a Nikon Eclipse Ci-L Light Transmitted Microscope (LTM) equipped with a Nikon DS-Fi3 high-definition colour microscope camera. Under the LTM, single yarns were separated, based on the differences in colour and shape, paying attention also to separate the weft and warp. The images obtained are reported in the Supplementary Materials (Appendix 1A).

Scanning Electron Microscopy observations were performed employing a Carl Zeiss Sigma VP Field Emission Scanning Electron Microscope (FE-SEM) equipped with EDS Bruker Quantax 200 probe used for elemental analysis. Analysis was performed in high vacuum (pressure around 10^{-6} - 10^{-5} mbar) with different magnifications (100x -250x--500x--5-000x and 10-000x) at 10keV. Samples were cut to fit in the microscope vacuum chamber, fixed with conductive tape and sputtered with Au for 30 seconds.

Apart from the red silk velvet, which was not analysed due to its peculiar weaving, the other silk samples were subjected to SEM-EDS analyses. Specifically, treatment 3 (immersion in MIBACT sanitising solution for 24h) and treatment 8 (immersion in 75% EtOH for 24h) were taken into consideration, based on the visual observation and the spectroscopic data. Changes on silk samples due to the treatments were evaluated in comparison to the untreated ones. EDS analysis were collected at 5000x magnification on all the area in order to be representative.

The white industrial and yellow silk can be considered as a new textile, while the Querini silk may represent an aged one with a compromised conservation state.

Further morphological characterization of the silk surface was carried out by using a Bruker Dimension ICON Atomic Force Microscopy (AFM) in tapping mode with a RTESPA-300 silicon cantilever (nominal spring constant ~40 N/m,

nominal tip radius ~8 nm, measured resonance frequency 325,3 kHz).

3D nanometric structure of silk and possible variations at the micrometric level before and after treatment were considered. Different areas of the two samples were investigated at different magnifications, ranging from 5 μm^2 to 1000 nm^2.

AFM analyses were conducted on tapping mode providing greatly magnified images of silk surface structure. Images of the white silk, untreated and after immersion in sanitising solution for 24 hours, have been compared. The analysis was performed on a portion of fabric rather than on a single thread (as reported by other literature studies) to test the possibility of investigating the unaltered sample [24,33]. The samples analysed were the same specimens investigated via scanning electron microscopy. Image acquisition and manipulation were performed by the proprietary software NanoScope Analysis.

2.3.2 Colorimetric measurements

Measurements were performed based on Colourimetric space CIELAB 1976 with a portable spectrophotometer (Konica Minolta CM-700d, Tokyo, Japan) equipped with CM-S100w (SpectraMagicTM NX, Tokyo, Japan) software; data were collected in SCI mode (Specular Component Included) and elaborated by Spectra Magic NX 6 software. A Teflon-based Spectralon metrological standard (Labsphere, North Sutton, NH, USA), diffusing 99% of incident light was used for calibration. The total colour difference, ΔE, was calculated according to the equation [34,35].

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

where ΔL*, Δa* and Δb* are the differences between the values obtained on the same sample, after and before the treatments. A positioning mask was used to place the measuring head (3 mm diameter) on the same area of the silk samples before and after treatments.

A variation of ΔE higher than 3 is considered detectable by the human eye [36–38].

2.3.3 Spectroscopic analyses

Infrared spectroscopy analyses were performed with a portable ALPHA II spectrometer (Bruker Optics) equipped with an Attenuated Total Reflection (ATR) modulus based on a single-bounce diamond ATR crystal. The spectra acquisition was performed over the range of 4000-400 cm^{-1} accumulating 128 scans at a spectral resolution of 4cm^{-1} [23]. An equivalent number of background scans were conducted before each measurement.

Raman spectra were collected with a Bravo portable Raman spectrometer by Bruker Optics. Spectra were collected in the wavenumber spectral range between 3200-300 cm^{-1} (resolution 10 cm^{-1}, scan time from 1s to 60s). The instrument is equipped with two lasers (758 and 852 nm) working simultaneously and it automatically sets its background by averaging three signals of the two sources. The first laser is dedicated to the acquisition of the Raman spectra in the first range, called the fingerprint region (170–2200 cm^{-1}), while the second one in the second range, the CH region (1200–3200 cm^{-1}) [39]. Laser power was below 100 mW for both sources. Spectral acquisition and manipulation have been performed by the proprietary software, OPUS (8.2.28 version). Baseline correction was applied on most of the acquired data [40]. Final plot of spectra and peaks assignation was done applying Origin 8.5 software [41].

3 Results

3.1 Assessment of the visual and morphological variations caused by treatments

Table 2 briefly illustrates the visual changes on the silk samples due to the different treatments and evaluated by contact microscope. Fig. 2 reports, specifically, the photos of the silk samples at 50x and 220x before and after immersion in MIBACT solution for 24h (t3), responsible of the most visible changes (see Table 2).

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Table 2

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visible morphological variation on the silk samples after the different treatments.

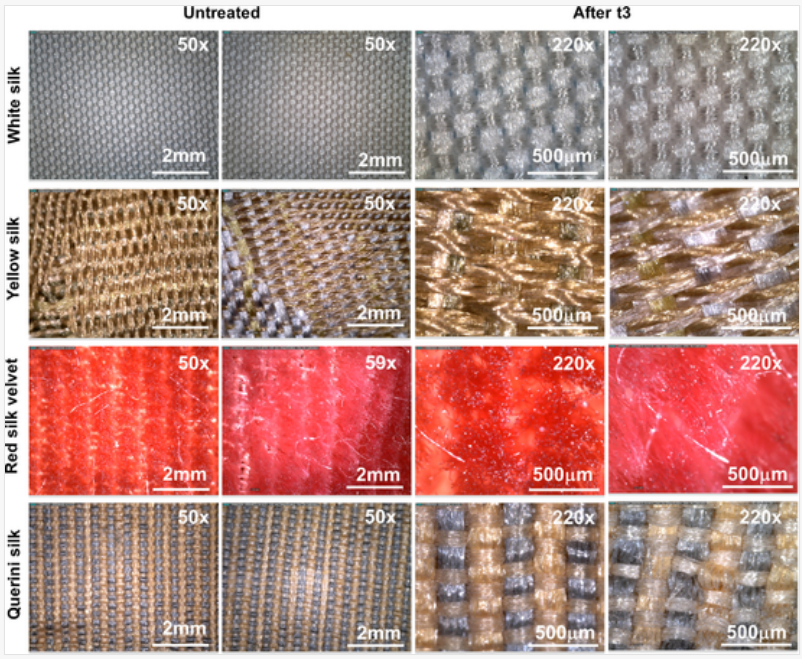
Type of treatment*	Silk sample			
	White silk	Yellow silk	Red silk velvet	Querini silk

t1	No changes	No changes	No changes	No changes
t2	No changes	Minor colour fading on some threads	Minor colour fading	Minor colour fading
t3	No changes	Consistent colour fading on some threads	Consistent colour fading	Consistent colour fading
t4	No changes	No changes	No changes	Colour appears slightly brighter
t5	No changes	No changes	No changes	Colour appears slightly brighter
t6	No changes	Consistent colour fading on some threads	Minor colour fading	Colour fading
t7	No changes	Consistent colour fading on some threads	Minor colour fading	Colour fading
t8	No changes	Consistent colour fading on some threads	Minor colour fading	Colour fading
t9	No changes	Consistent colour fading on some threads	Minor colour fading	Colour fading

*t1vapur exposure to MIBACT sanitizing solution for 10 days; t2- immersion MIBACT solution for 30 min; t3-immersion in MIBACT solution for 24h; t4-immersion in deionized water for 24h; t5-immersion in absolute EtOH for 24h; t6-immersion in EtOH 50% for 24h; t7-immersion in EtOH 70% for 24h; t8-immersion in EtOH 75% for 24h; t9-immersion in EtOH 79% for 24h

alt-text: Fig 2:

Fig. 2



silk samples observed via contact microscope (50x and 220x) before and after treatment t3 (immersion in sanitising solution for 24h).

The white silk was the only fabric that did not show clear visible changes after the treatments; in all the other samples, the most evident effect of the treatments consists in a colour fading. In fact, most of the solutions used for the immersion tests also changed their colour, probably due to loss of dye from the textiles (see paragraph 3.2).

The vapour treatments with the MIBACT sanitizing solution (t1) did not affect the visual aspect of the fabrics. The immersion in the sanitizing solution (t2, t3), on the other hand, was responsible of visual changes, in particular colour fading, more evident for prolonged treatments (t3). Residues of BZK were not, however, clearly visible on the yards.

Independently from the percentage of water/ethanol blends, contact microscopy did not show clear visual differences among the samples treated.

The immersion in pure water (t4) or pure EtOH (t5) did not change the visual aspect of the silks apart for the Querini one, which resulted slightly brighter, probably due to the removal of the dust present on the fabric. For the yellow silk, specifically, it was also possible to appreciate a different visual change of the werf and warp yellow threads. Two type of silks (Bombix mori and Tussah) and the presence of vegetable fiber (such as cotton) were, in fact, here hypothesised (see Supplementary Materials – Appendix 1A) [18,31].

Based on the preliminary visual observation with the contact microscope, SEM-EDS analysis were performed of the untreated silk samples and on the samples after immersion for 24 hours in the MIBACT solution (t3) to evaluate possible visible changes. Fig. 3 reports the SEM analysis (500x, 5000x, 10000x) and the related EDS for the white silk, the yellow silk and the Querini silk. The red silk velvet was not analysed due to the peculiar weaving. In addition to the t3, also the samples after immersion in EtOH 75% (t8) were analysed (see Supplementary Materials – Appendix 1C).

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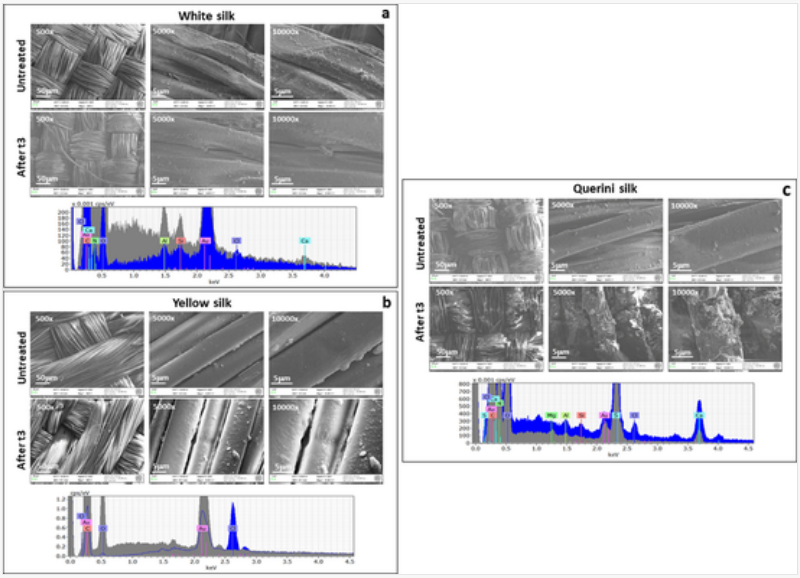
Fig. 3



SEM-EDS images of the white silk (a), yellow silk (b) and Querini silk (c) before and after immersion in sanitising solution for 24 hours (t3).

After treatment 3, all silk samples obviously showed the presence of Cl due to residues of BZK over the fibres, as the samples were not rinsed and left to dry naturally. Apart for the Querini silk, where deposition of BZK on the fibers was visible, BZK might have been homogenously absorbed by the other silk fabrics as not clear differences are visible in comparison to the untreated one: formation of salt or increase of particles on the fibers were not evident. In the specific case of the Querini silk, the SEM image, taken at 5000x, highlighted an increase of broken fibres with the formation of micro fracturing and detachments. The white and the yellow silk did not clearly show visual modification of the fibres. They did, however, seem slightly smooth indicating maybe a loss of striation after t3. The EDS of the Querini also highlighted the presence of S, Ca, Mg, Al, and Si probably related to the dust. In particular, S and Ca could be linked to the presence of gypsum supported by IR analysis of the same samples (see paragraph 3.3.1).

AFM analysis performed of the same samples pointed out the presence of valleys and craters on the untreated samples. These were less evident after t3, as highlighted by the line profiles of the white silk, reported here as an example (Fig. 4). In the treated samples, several emerging structures are visible, probably due to residues of benzalkonium chloride, as evidenced by EDS spectra.

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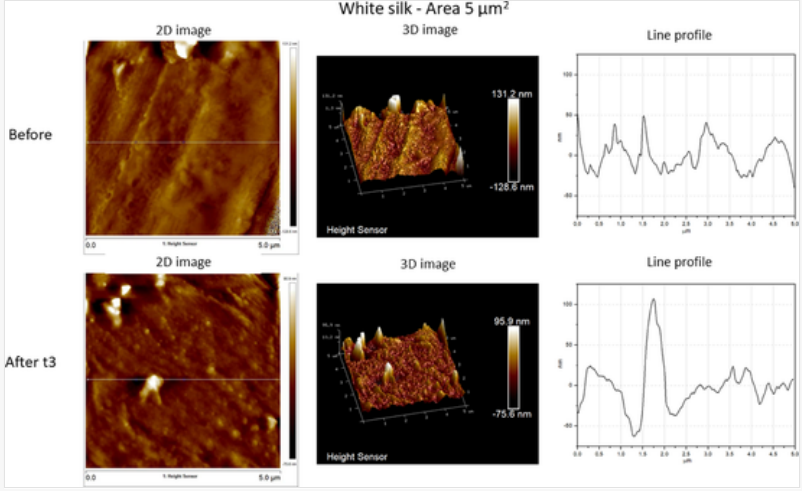
Fig. 4



results from AFM analyses performed on the white silk before and after immersion in sanitising solution for 24hours (t3); 2D and 3D images are presented together with a line profile for the 2D image.

The fabrics were analysed by SEM-EDS also after treatment 8 (immersion in 75% EtOH for 24h) and the related SEM images are reported in the Supplementary materials (Appendix 1C). In general, the t8 did not show evidence of visible variation on fibers. After t8, silk fibers visually appeared smoother than the untreated ones, with a minor presence of particle on the surface. This could be due to a wash effect as the samples were immersed in 75% EtOH for 24h.

3.2 Colour variations after treatments

Table 3 briefly summarises the colour variations in terms of ΔE of the silk samples after the treatments, while Table 1B, in the Supplementary Materials, reports the related colourimetric values.

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Table 3

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Resume of the colour variation based on DE values of the silk samples after the different treatments: no colour change (ΔE<1); minor colour change (ΔE<5); moderate colour change (5<ΔE<10); major colour change (ΔE>10).

Type of treatment*	Silk sample			
	White silk	Yellow silk	Red silk velvet	Querini silk
t1	Minor	No	Moderate	Moderate
t2	No	Moderate	Moderate	Minor
t3	Minor	Major	Major	Minor
t4	Minor	Minor	Minor	Minor
t5	Minor	Minor	Minor	Minor
t6	Minor	Minor	Minor	Moderate
t7	Minor	Moderate	Major	Minor
t8	Minor	Major	Moderate	Major
t9	No	Major	Major	Minor

Few common tendencies could be found after immersion treatments for the coloured silks, as reported in Fig. 5. before and after the different treatments.

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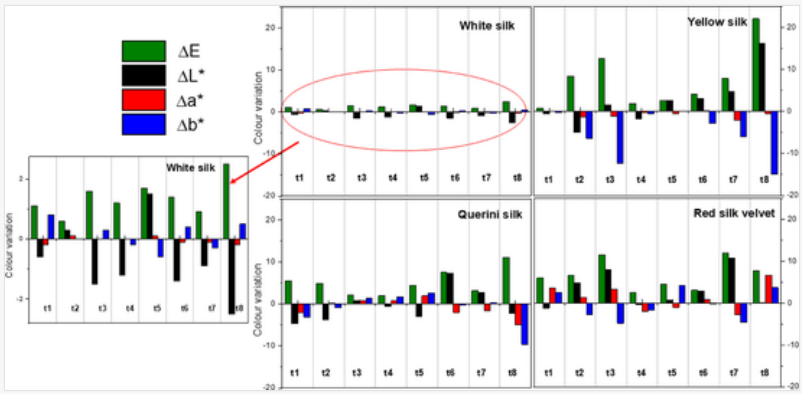
Fig 5



variation of colour components for each type of treated silk samples.

The treatments affected the colour of the silk samples in different ways depending on the nature of the solutions and of the samples.

Among the fabrics, the white silk showed only minor colorimetric changes ($1<\Delta E<5$) with a reduction mainly on lightness (negative ΔL^*), especially after immersion in ethanol/water 75% blend (Fig. 5). This loss of lightness of the white silk may be related to possible interactions of alcohol with the secondary structure of silk [30,42].

The treatment t1 (vapour exposure for 10 days to MIBACT solution) showed minor colour changes also for yellow silk ($\Delta E=0.8$) while the red silk velvet ($\Delta E=6.0$) and the Querini silk ($\Delta E=5.5$) had a higher ΔE variation resulting less bright.

Among the two immersion tests for the MIBACT sanitizing solution (t2, t3), as expected, the 24h treatment (t3) gave the more consistent ΔE variation, apart for the Querini silk. This fabric is characterized by threads of different colour that did react differently to the treatments, as showed also by the contact microscopy (Fig. 2); this may affect the colour evaluation. The immersion for 24h (t3) resulted to be the most affecting treatment for the yellow and the red silk velvet in terms of ΔE with a value of 12.6 and 11.5, respectively.

In general, pure water and pure EtOH gave minor variation of ΔE and ΔL^* with respect to water/alcohol blends, where part of the colour faded staining the solutions. The t8 (75% EtOH) gave the most significant variation of ΔE, apart for the red silk. The important colour variations for the yellow silk after t8, with values up to 20 (Fig. 5), may be also partially due to the weaving structures, as highlighted by the contact microscope the weft and warp behave in a different way.

To properly understand if BZK did have an influence on the colour variation, the white silk was considered as this was not giving colour fading. The colorimetric values after t3 compared to ones after t4 (pure water) were almost comparable. BZK residues did not result to significantly affect the silk colour.

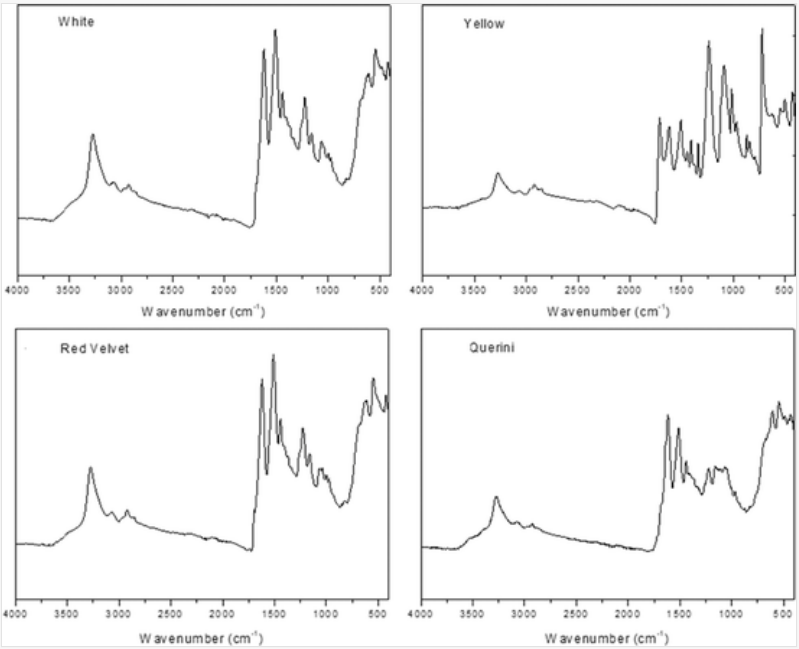
3.3 Assessment of the Chemical impact of the sanitizing solutions by Spectroscopic analyses

3.3.1 FTIR Analyses

Fig. 6 shows the FTIR-ATR spectra of the four types of untreated fabric.

alt-text: Fig 6:

Fig. 6



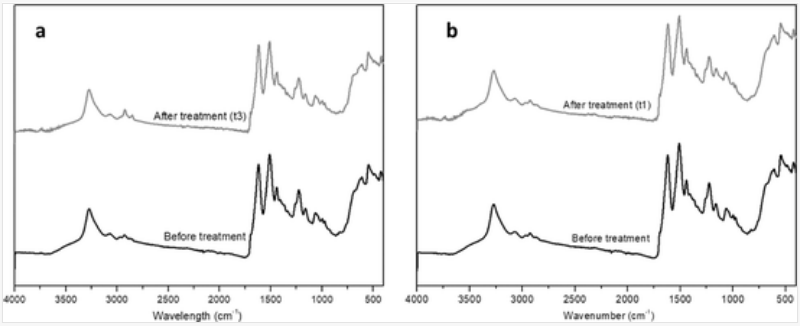
FTIR- ATR spectra of the four silk samples before treatments.

The collected infrared spectra appear similar and, apart from the typical signals characterizing silk (e.g. signals at 3279 cm^{-1} of NH vibration, 1620 cm^{-1} and 1510 cm^{-1} of amide I and II respectively, 1441 cm^{-1} of CH_2 and CH_3 bending in alanine, 1227 cm^{-1} of amide III, 1065 cm^{-1} of CH_3 rocking) [19,23,43], no specific peaks related to other compounds (such as colourants, mordants, etc.) could be easily identified. The yellow silk presented minor differences in peaks intensity and positions, probably related to the production process. In particular, at 1715 cm^{-1} and in the range between 1100-700 cm^{-1}, few absorption peaks could be detected and may be associated to the presence of cellulosic fibres (such as cotton also observed by Light Transmitted Microscopy in the Supplementary Materials – Appendix 1A): 1093, 1012, 870, 840, 722 cm^{-1} [44–46].

In the case of the immersion test in sanitising solution for 24h (t3), the presence of benzalkonium deposits (signals at 2920, 2850 and 1004 cm^{-1}) were detected, in agreement with the results of SEM analysis [47,48]. Apart from this, after treatment t3 (Fig. 7a) no other relevant modifications to silk characteristic peaks could be observed. The presence of BZK on silk was not detected after treatment t1 (Fig. 7b), exposure to the sanitising solution vapours for 10 days was probably too short.

alt-text: Fig 7:

Fig. 7

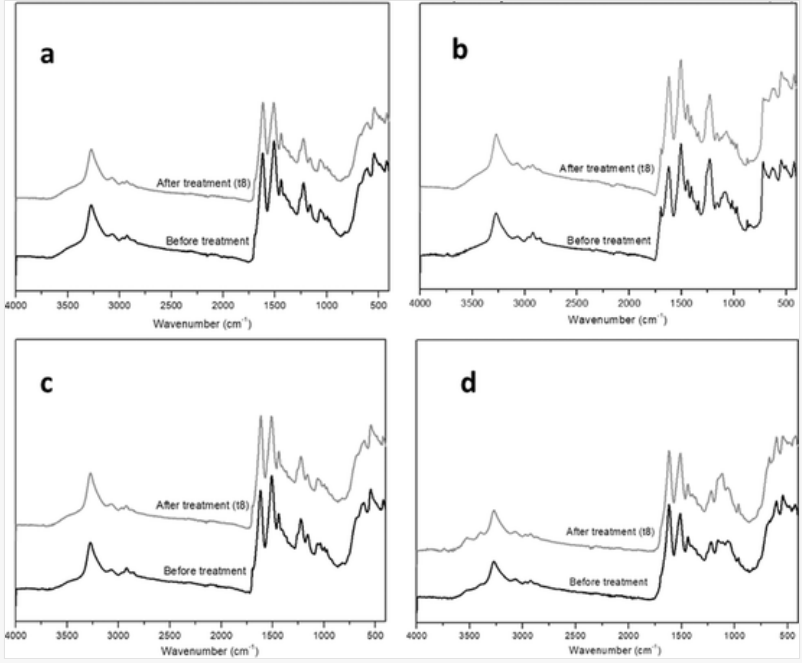


a) FTIR-ATR spectra of the white silk before and after immersion in the sanitising solution for 24 hours (t3); b) FTIR-ATR spectra of the yellow silk before and after exposure to the sanitising solution vapours for 10 days (t1).

As reported in the literature, possible variations in the silk characteristic vibrations -due to the structural change of peptide planar bonds induced by ethanol- could be expected in the single bond region (3600-3000 cm^{-1}) for CH stretching signals, and in the NH bending region (1650-1580cm^{-1}) [30,42]. In our case, no significant modifications were detected on silk fabrics after treatments with ethanol 50-79% (Fig. 8), even despite the observed colorimetric variations.

alt-text: Fig 8:

Fig. 8



FTIR-ATR spectra of silk samples before and after immersion in 75% ethanol for 24h (t8): a) White silk; b) Yellow silk; c) Red velvet; d) Querini silk.

3.3.2 Raman Analyses

Raman spectra of all the untreated silk samples showed the characteristic peaks of silk such as: three intense peaks between 2990 and 2875 cm^{-1} attributed to the CH_3 stretching; the stretching of amide I at 1667 cm^{-1}; a signal related to phenylalanine at 1609 cm^{-1}; the bending of CH_2 and CH_3 at 1451 cm^{-1}; the amide III bending signals at 1269 cm^{-1} and 1232 cm^{-1}; the CN stretching at 1087 cm^{-1}, and, finally, the characteristic tyrosine and tryptophan triplet at 880-850-830 cm^{-1} [23,43,49].

Next to these signals, in the red silk velvet spectrum, the peaks at 1606 cm^{-1}, 1586 cm^{-1}, 1324-1302-1275-1251 cm^{-1} and at 1206 cm^{-1} were attributed to madder or studio red, probably used as colourant [50].

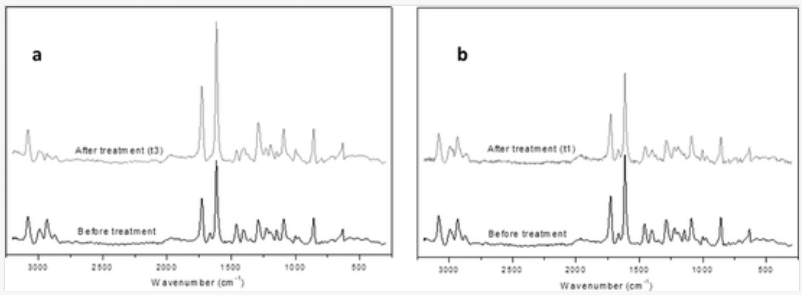
In the case of the yellow silk, as already pointed out by FTIR-ATR, characteristic peaks associated to the possible presence of cellulosic fibres could be identified: 1727 cm^{-1}, 1614 cm^{-1}, 1290 cm^{-1} [49]. Specific peaks related to the presence of colourants were, on the other hand, hard to identify.

In the Querini silk, the Raman spectra presented few characteristic signals not belonging to silk: 1550-1500 cm^{-1}, 1328 cm^{-1}, 1271 cm^{-1} and 906 cm^{-1}. These signals could be probably related to the presence of phthalocyanine green used as dye [51].

The comparison of Raman spectra collected after treatments t3 and t1 provided some interesting results. After immersion in the sanitising solution for 24h (t3), as previously seen in the FTIR-ATR spectra, Raman analyses confirmed the presence of benzalkonium chloride thanks to the increasing peak intensity around 1004 cm^{-1} (Fig. 9a) [48]. This signal was detected only after immersion in sanitising solution, while no relevant modifications were observed after exposure to sanitising solution vapours (t1) (Fig. 9b).

alt-text: Fig 9:

Fig 9

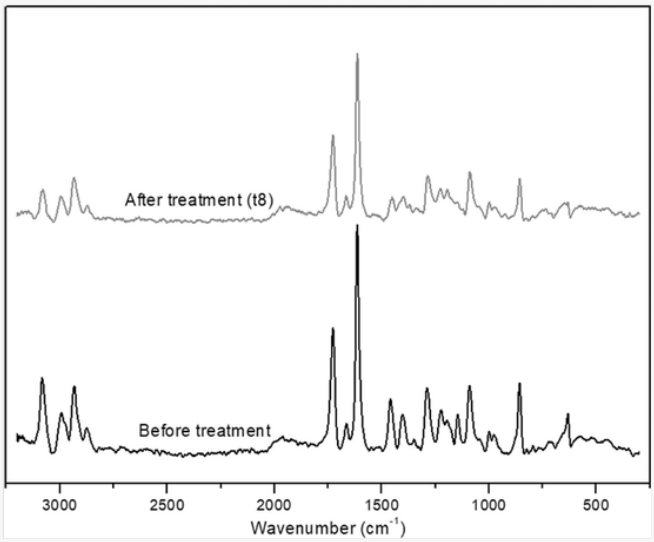


a) Raman spectra of the yellow silk before and after immersion in sanitising solution for 24 hours (t3); b) Raman spectra of the yellow silk before and after exposure to sanitising solution vapours (t1).

After immersion in ethanol/water blends, silk samples did not show relevant Raman variation. Only in the case of the yellow silk and the red silk velvet minor modifications of the peaks, probably associated to the loss of colourant, could be detected. Specifically, after the treatments (e.g. t8) the intensity of the peaks at 1462cm^{-1} and 1406 cm^{-1} for the yellow silk (Fig. 10) and of the signals between 1350 cm^{-1} and 1240 cm^{-1} for the red silk velvet decreased [50,52].

alt-text: Fig 10:

Fig 10



Raman spectra of the yellow silk before and after immersion in 75% ethanol for 24h (t8).

Raman analyses confirmed that the different treatments applied did not give significant variations, at least under these experimental conditions. Nevertheless, it was possible to observe minor variations in the intensity of peaks probably related to dyes. Signals associated with residues of benzalkonium chloride after immersion in sanitising solution were detected, in accordance with FTIR-ATR analysis.

4 Discussion

As for many ~~e~~Cultural ~~h~~Heritage materials, in the case of silk fabrics important characteristics (such as age, conservation state, production and dying techniques) may play a crucial role on the interaction with sanitizing products.

The MIBACT sanitizing solution (water-ethanol-benzalkonium chloride mix) was here considered as this was indicated by IMC – Superintendence Roma to be used in museums and churches. Next to this, different water-alcohol blends were considered, based on the range of commonly available sanitizing products.

Apart for the white silk, all the coloured silks (a yellow recently produced silk, ~~:~~ a red velvet silk and an aged silk) showed visible changes in particular when water and alcohol were mixed and when immersed in MIBACT solution

(t3). The major effects of the ethanol/water blends were probably due to -H bond stabilization of the mixture, as reported in the literature [53], which extends the interaction times and its effects on textiles [8]. The colour faded into the solutions and it was possible to appreciate a different sensitivity of yarns depending probably to the dye used and/or production technique.

FTIR-ATR and Raman analysis on the silks confirmed the presence of BZK after t3 and showed mainly minor variations on the characteristic silk peaks after all treatments. As reported in the literature, possible variations in the silk characteristic vibrations -due to the structural change of peptide planar bonds induced by ethanol- could be expected in the single bond region (3600-3000 cm^{-1}) for CH stretching signals, and in the NH bending region (1650-1580 cm^{-1}) [30,42]. In our case, no significant modifications were detected after treatments with ethanol 50-79%, even despite the observed colorimetric variations. Two plausible hypotheses could explain this. The first is that, under these conditions, the interaction silk-alcohol did not produce relevant chemical changes observable via FTIR-ATR, even after 24 hours of immersion in ethanol/water blends. The second one might be related to the application of FTIR-ATR technique on soft materials, as highlighted by Badillo-Sanchez [54]. The pressure exerted by FTIR-ATR on silk may lead to record a signal from the bulk rather than the surface itself, differently affected by the interactions with the solutions [54].

The SEM-EDS analysis and FTIR-ATR obviously confirmed the presence of BZK on the silks as these were intentionally not rinsed after immersion test. According to SEM images, AFM analysis seemed to reveal a microscopic visual modification of the fibers induced by t3 [24].

5 Conclusions

Due to the pandemic, the use of alcohol-based sanitising products in ~~h~~Heritage sites opened new questions regarding its possible effects on artifacts. The focus of this study was put specifically on silk, being this material extremely delicate and widely diffused in museums and historic houses.

Vapour exposure for 10 days and immersion tests (30min and 24h) were carried out. Immersion tests are far from accidental, but this scenario was intentionally exacerbated to understand if the use of sanitising products represents a real conservation risk for silk. The MIBACT recommended sanitising solution (75% ethanol, 20% water, 5% benzalkonium chloride) was taken as the reference product. Tests with blends of water and ethanol in different concentrations were also performed.

Considering the results obtained, a few conclusions can be drawn.

- Vapour test with MIBACT solution did not give relevant spectroscopic changes, probably the exposure time was too short. However, the red silk velvet and Querini silk did show colourimetric variations.
- Within the employed experimental conditions, minor modifications were detected with IR and Raman despite the known effects of alcohols on proteins and the colour variation observed.
- The consistent colour variations of the coloured silks, observed after immersion treatments, were mainly caused by ethanol/water blend within a concentration range of 70%-79% and were only partially influenced by the presence of benzalkonium chloride.
- As it was easy to predict after the immersion tests in MIBACT solution, IR, Raman and SEM-EDS analysis evidenced the presence of benzalkonium chloride on samples. Samples were intentionally not rinsed presuming that accidental spill also by visitors may not be noticed and may get to naturally dry on the fabrics.

This research highlighted no evident morphological and chemical modifications related to the use of sanitizing solutions on silk but showed other drawbacks such as colour modification, equally important when referring to cultural objects. A change in colour, as showed by this study, especially if limited to a spot or a partial area, would represent a detrimental effect. Even though BZK reduces material surface tension and has antimicrobic action, if possible, it should not be added to sanitising as it can deposit on fibers affecting their micro-structure. Depending on the microclimate conservation condition (T, RH%), BZK may affect the surface tension facilitating water condensation on silk fibers and possible degradation processes.

While chemical modifications were difficult to detect or would need longer treatment times, we cannot exclude changes in mechanical behaviour of the textiles. The application of mechanical testing to determine potential changes in physical properties of silk fibers and ageing experiments, to better understand the long-term effect, especially of BZK that appears to be deposited on the fabric, should be considered.

Q2 Author contributions

Conceptualization E.Z.; methodology E.Z., B.F., E.B.; investigation E.Z., B.F., E.B., F.R.; data curation E.Z., B.F., E.B., F.R.; writing – original draft preparation E.Z., B.F., E.B.; writing – review and editing E.Z., B.F., E.B., F.R.;

supervision E.Z. All authors have read and agreed to the published version of the manuscript.

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Declaration of Competing interest

The authors declare no conflict of interest.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.culher.2021.06.012.

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Highlights

- Sanitisations need to be considered for Cultural Heritage preservation.
- The fragility of silk, widely used for interior decorations, is often underestimated.
- To simulate possible interactions with sanitising solutions immersion and vapour tests performed.
- No relevant chemical variations were detected by IR and Raman spectroscopy.
- Consistent colorimetric variations were highlighted after treatments.

Appendix Supplementary materials

Multimedia Component 1

alt-text: Image, application 1

Queries and Answers

Q1

Query: Please confirm that givennames and surnames have been identified correctly.

Answer: Yes

Q2

Query: We find that the roles provided for the all authors do not match the list of acceptable roles. Please choose a role from the below list for authors:-Conceptualization, - Data curation, - Formal analysis, - Funding acquisition, - Investigation, - Methodology, - Project administration, - Resources, - Software, - Supervision, - Validation, - Visualization, - Writing - original draft, - Writing - review & editing.

Answer: E.Z. Conceptualization, Methodology, Review & editing, Resources, Supervision

E.B. Data curation, Investigation, Methodology, Review & editing

B.F. Data curation, Investigation, Methodology, Writing original draft

F.R. Investigation, Methodology, Review &Editing

All authors have read and agreed to the published version of the manuscript.

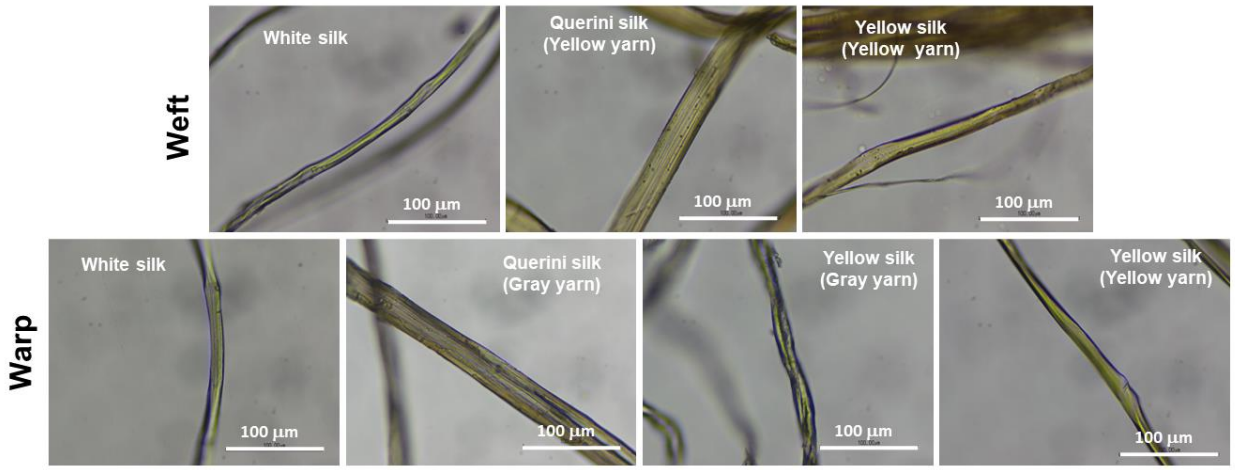
SUPPLEMENTARY MATERIAL

Appendix 1A Silk samples identification via Transmitted Light Microscopy (TLM)

The observation of the silk fabrics under the microscope evidenced the possible presence and/or use of different yarns in particular in the case of the Querini and the yellow silk. Under the microscope, singles yarns were separated from each fabric and identified using a Nikon Eclipse Ci-L Light Transmitted Microscope (LTM) equipped with a Nikon DS-Fi3 high-definition colour microscope camera. Fig. 1 A reports the images obtained with a magnification of 40x. For the red silk velvet, it was not possible to obtain a significant sample due to the peculiar structure of the fabric.

Apart for the yellow silk, all fabrics are realised using silk for weft and warp. Based on the images obtained by TLM (Fig. 1A) it is possible to say that the silk fabrics were realised using mainly degummed silk characterised by independent single smooth and structureless filaments. Raw silk threads commonly consist of two single filaments surrounded by the gum, that can crack and be irregularly attached to the fibroin filaments [1,2].Moreover, next to the most common Bombyx mori silk threads, the presence of wild silk (i.e. Tussah) cannot be excluded in the case of the Querini silk. Under the microscope, these threads resulted unevenly thick and band shaped with fine vertical stripes which can be attributed to the fibre fibrillar structure. In the case of the Qiuerini silk it is also possible to appreciate differences in terms of colour between the yellow and the grey threads. Peculiar is the case of the yellow silk where it was possible to separate three different yarns different for colour and aspect. Specifically, a yellow thread was used for the weft while two different yarns were used for the warp: a yellow and a gray one. The gray yarn can be identified as cotton due to the characteristic twists and distortions [1,2]. The presence of a vegetable yarn, probably cotton, was also pointed out by FTIR-ATR.

Fig. 1A: Images of the threads obtained by Transmitted Light Microscopy for the white silk, yellow silk and Querini silk.



Appendix 1B Colourimetric measurements

Table 1B reports the colorimetric changes recorded for each type of silk after the different treatments.

Table 1B: colourimetric data relatives to the silk samples before and after treatments.

TREATMENT	ΔE	ΔL*(D65)	Δa*(D65)	Δb*(D65)
White silk				
t1	1.1	-0.6	-0.2	0.8
t2	0.6	0.3	0.1	0.0
t3	1.6	-1.5	0.0	0.3
t4	1.2	-1.2	0.0	-0.2
t5	1.7	1.5	0.1	-0.6
t6	1.4	-1.4	-0.1	0.4
t7	0.9	-0.9	-0.1	-0.3
t8	2.5	-2.5	-0.2	0.5
t9	0.8	-0.7	-0.2	0.4
Yellow silk				
t1	0.8	-0.6	0.0	-0.3
t2	8.4	-4.9	-1.3	-6.4
t3	12.6	1.6	-1.1	-12.4
t4	1.9	-1.8	-0.3	-0.5
t5	2.7	2.7	-0.6	0.0
t6	4.2	3.1	0.2	-2.8
t7	7.9	4.8	-2.0	-6.0
t8	22.1	16.2	-0.5	-15.0
t9	16.6	10.7	0.8	-12.6
Red silk velvet				
t1	6.0	-1.2	3.6	2.5
t2	6.6	4.8	1.4	-2.7
t3	11.5	8.0	3.3	-4.8
t4	2.6	-0.4	-2.0	-1.7
t5	4.5	0.8	-1.0	4.3
t6	3.1	2.9	0.9	-0.2
t7	12.0	10.8	-2.7	-4.6
t8	7.7	0.2	6.7	3.7
t9	13.4	10.2	-5.5	-6.9
Querini Silk				
t1	5.5	-4.7	-2.0	-3.1
t2	4.9	-3.7	0.2	-0.9
t3	2.2	0.8	0.8	1.4
t4	2.0	-0.6	0.8	1.8
t5	4.5	-3.0	2.0	2.6
t6	7.6	7.3	-2.0	-0.3
t7	3.2	2.8	-1.6	0.3

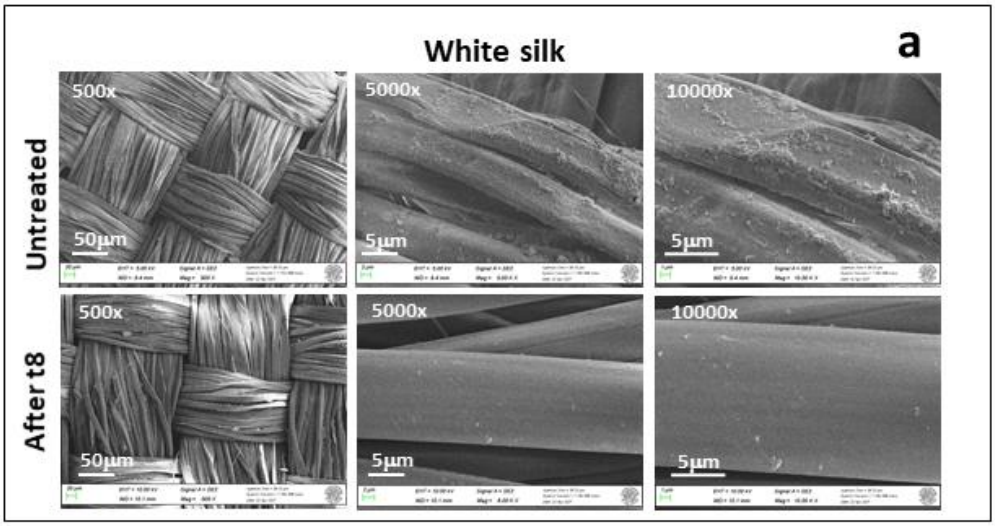
t8	11.1	-2.2	-5.0	-9.6
t9	2.4	1.1	-2.0	-0.6

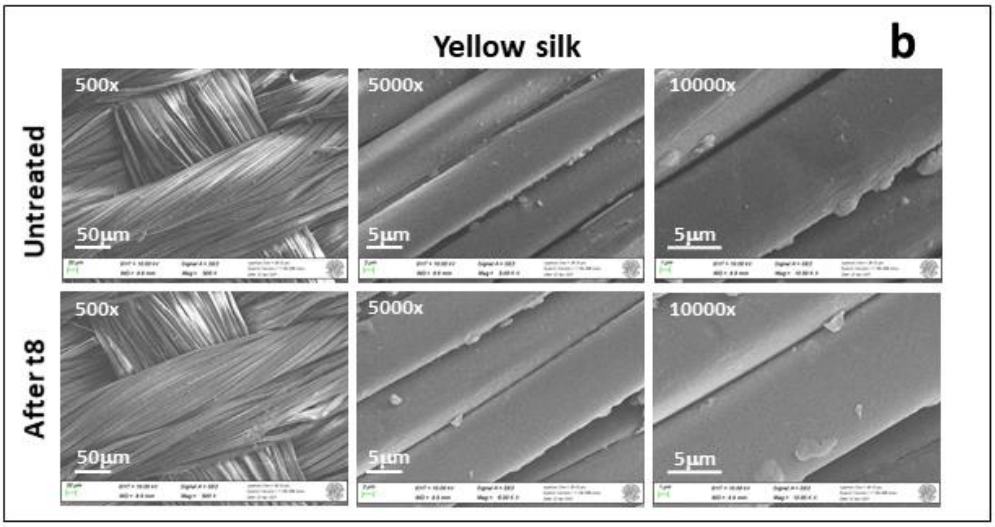
*t1vapur exposure to MIBACT sanitizing solution for 10 days; t2- immersion MIBACT solution for 30 min; t3-immersion in MIBACT solution for 24h; t4-immersion in deionized water for 24h; t5-immersion in absolute EtOH for 24h; t6-immersion in EtOH 50% for 24h; t7-immersion in EtOH 70% for 24h; t8-immersion in EtOH 75% for 24h; t9-immersion in EtOH 79% for 24h.

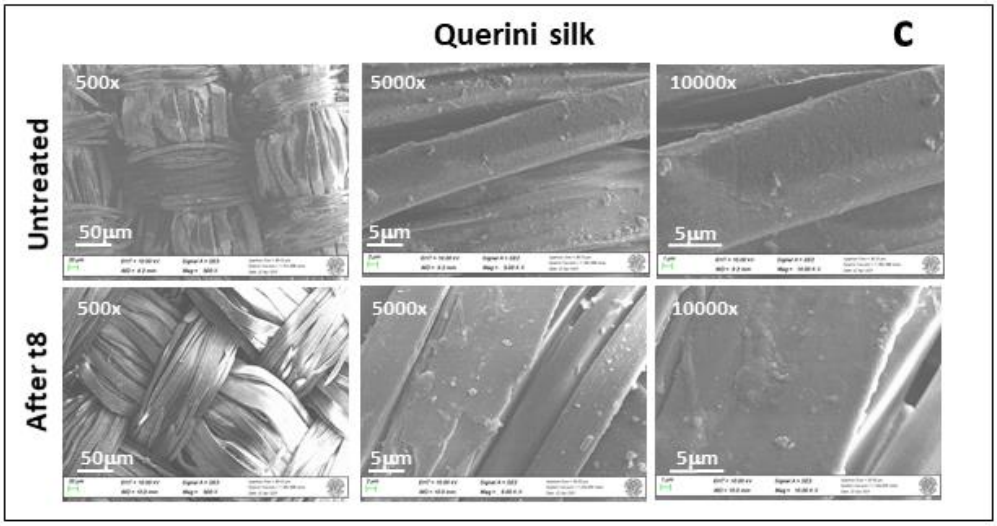
Appendix 1C SEM-EDS analyses

Fig. 1C shows the SEM images and associated EDS analysis after t8 (immersion in 75% EtOH for 24h) collected for the white silk. the yellow silk and the Querini silk. White and yellow silk appear smoother: this could be due to a wash effect as the samples were immersed in 75% EtOH for 24h. Clear evidence of possible permanent microstructural changes of fibers is however difficult to detect. In the case of the Querini silk. which was in a bad conservation state and covered by dust. the alcohol immersion did not seem to affect the fibers: no clear increase of broken fibers. micro fracturing or loss of materials. The treatment most probably mainly removed the dust as the silk fiber results more evident (500x).

Fig. 1C: SEM images (500x, 5000x, 10000x) of the white (a), yellow (b) and Querini (c) silks collected on the untreated and after t3 (immersion in 75% EtOH solution for 24h).


White silk
a
Untreated
After t8
500x
5000x
10000x
50µm
5µm


Yellow silk
b
Untreated
After t8
500x
5000x
10000x
50µm
5µm


Querini silk
c
Untreated
After t8
500x
5000x
10000x
50µm
5µm