Paolino *et al. Heritage Science* (2024) 12:334
https://doi.org/10.1186/s40494-024-01442-8

Heritage Science

REVIEW **Open Access**

Greener solutions for biodeterioration of organic-media cultural heritage: where are we?

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Abstract
Eco-friendly decontamination treatments on works of art made from organic materials are of growing interest. The high risks to human health and the environment associated with traditional biocides (*e.g.* ecotoxicity, development of biotic resistance) have made it necessary to search for safer alternatives, also looking at the past but innovating it. The current state of the art is explored here, delving into the literature on the topic from 2000 to today, and outlining trends in terms of the most tested artistic supports and types of published research (in vitro/in vivo). An overview of the characteristics and mechanisms of biodegradation processes on different types of organic products and on the microorganisms mainly involved is thus provided. The main chemical-physical action techniques tested are illustrated and their practical-applicative aspects are discussed on the basis of evidence from case studies. Taking stock of the actual situation, literature consultation highlights that if on the one hand research is advancing rapidly towards the discovery of new ecological and safe solutions, on the other hand these are often biocidal treatments whose protocols have yet to be explored and validated.

Keywords Organic-media cultural heritage, Biodeterioration, Chemical treatments, Natural products, Green solutions

Introduction

Bio-colonization is one of the main causes of the degradation of artistic artifacts, and as a result, it is a recurring intervention in art restoration [1, 2]. Biocidal treatments for disinfection from microbial agents are routinely carried out using products based mainly on quaternary ammonium salts (QACs), compounds widely used in formulations for hygienic and disinfectant purposes in various industrial sectors that represent a reference commercial product in the restoration field. However, some critical issues are emerging regarding the use of these products, such as safety and eco-toxicity profiles, as well as the impact on the development of bio-resistance, which numerous recent studies have focused on [3]. For these reasons, research in the past twenty years has increasingly deepened alternative solutions to treat microbial colonization, aiming to reduce their impact on human health and the environment. From the literature, it is possible to identify two macro-categories of intervention for carrying out greener decontamination treatments: the first exploits a chemical mechanism of action, using substances with biocidal activity to be applied on the support that inhibits microbial growth and prevents its reappearance [4]. These substances, as will be further explored in this paper, can be organic or inorganic and may intervene at different stages of the microorganism's

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metabolic cycle. The second category involves the use of physical disinfection techniques, such as exposure to radiation or plasma [5]. The examination of the literature reveals that numerous studies concerning the utilization of natural biocides are centered on inorganic-based historical-artistic manufacts, primarily focusing on stone materials found in mural paintings, mosaics, architectural surfaces, and similar items [6]. This work instead aims to focus attention on organic-media artistic objects, a category that includes a wide variety of supports including cellulosic ones (artifacts on paper and derivatives, textiles based on plant fibers, wooden supports), keratinic ones (parchment artifacts, leather supports, textiles made of animal fibers, composite materials), and finally polymeric supports of synthetic origin that characterize contemporary artistic production. Organic artistic supports are often assemblies of heterogeneous materials, as in the case of canvas and easel paintings, parchment volumes, as well as ethnographic or natural history artifacts: this condition favors colonization by microbial consortia that act synergistically on all the different substrates [7–9] Hence, the aim of this review is to assess the current state of decontamination techniques applied to these manufacts that imply the use of chemical and physical protocols, while also examining the types of artifacts that have undergone more advanced research and identifying areas where information is lacking. Since the 2000s, studies on green treatments in cultural heritage conservation have increased significantly, but they are not homogeneous in the distribution of analyzed support typologies or the protocols experimented with, highlighting a differentiated interest in each topic.

The processes of degradation involved in contaminated substrates will also be examined, along with the *genera* most frequently isolated in the considered case studies, and the mechanisms that determine the biocidal action against microorganisms.

Finally, this analysis will reveal opportunities for further research on the subject, based not only on the results achieved in terms of effectiveness but also on practical feasibility.

Literature trends on the topic

To have a clear vision of the state of the art on the topic, two online search platforms, Science Direct and Scopus, were consulted and the following criteria were employed:

- Only peer-reviewed original articles and literature reviews in English were selected, excluding conference papers, book chapters, and thesis works.
- The chronological range taken into consideration span from January 2000 to March 2024.
- Keywords were chosen based on the main categories of biocidal treatments investigated here, namely: nanostructured materials, natural extracts, ionic liquids, gamma radiation, and low-temperature plasma. Keywords were also selected starting from organic-media typology: painting, plastic, paper, wood, textile and leather.

Keywords were entered into the two platforms (as described in Table 1), utilizing the search setting

Table 1 Literature collection: keywords used for research on Scopus and Science Direct database

Scopus				Science Direct			
< keywords >		***< keywords >***		***< keywords >***		***< keywords >***	
< plant material + cultural heritage >	[84]	< green biocide + painting >	[10]	< plant material + cultural heritage + biocide >	[153]	< green biocide + painting >	[255]
< essential oil + cultural heritage >	[114]	< green biocide + plastic >	[10]	< essential oil + cultural heritage + biocide >	[156]	< green biocide + plastic >	[81]
< nano-material + cultural heritage >	[147]	< green biocide + paper >	[44]	< nano-material + cultural heritage + biocide >	[81]	< green biocide + paper >	[249]
< plasma + cultural heritage >	[126]	< green biocide + wood >	[20]	< plasma + cultural heritage + biocide >	[45]	< green biocide + wood >	[168]
< gamma radiation + cultural heritage >	[55]	< green biocide + textile >	[11]	< gamma radiation + cultural heritage + biocide >	[55]	< green biocide + textile >	[41]
< Ionic Liquids + cultural heritage >	[18]	< green biocide + leather >	[1]	< Ionic Liquids + cultural heritage + biocide >	[40]	< green biocide + leather >	[17]
	Total [544]		*Total* [96]		*Total* [515]		*Total* [811]

In brackets [n] are reported the number of results

Selected papers [137]

"Title-Abstract-Keywords"; results were filtered for applications and case studies dedicated to organic supports. Finally, bibliographies of all collected papers were reviewed, and relevant studies were selected using the "snowball" methodology as previously reported in literature [6].

The collected literature was further categorized by year of publication, type of organic media, and theoretical/experimental study in vivo/in vitro.

It is evident that from the 2000s to the present research has increasingly focused on alternative solutions for the decontamination treatment of artistic objects on organic support, paying particular attention to the use of antimicrobial substances with chemical action (Fig. 1). Specifically, among these, the use of natural extracts stands out (as mentioned previously, mainly represented by essential oils), followed by experiments involving the use of nanomaterials. Physical techniques are also increasing in frequency, especially for the use of gamma radiation.

However, experimental procedures are not evenly distributed among different types of organic support: among the most extensively tested materials there are paper and wood supports (Fig. 2). It should be noted that cellulose-based supports (such for books and archival documents) are often characterized by a simpler composition, they

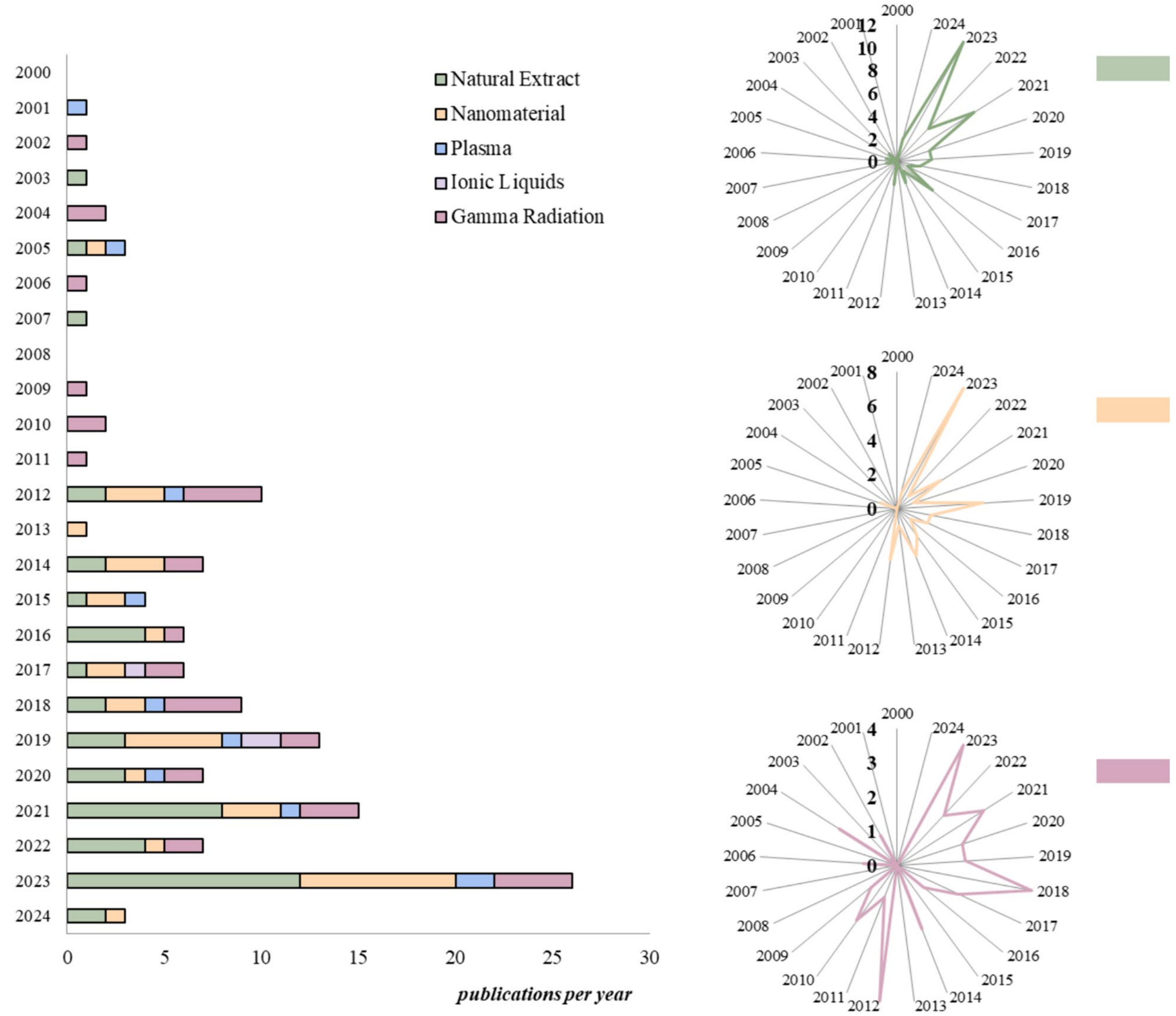

Fig. 1 Number of scientific papers published per year divided per green biocidal treatment on organic-media cultural heritage. Radar charts have been constructed to show the growing interest over the years in the application of strategies based on 🟩 natural products; 🟧 nanomaterials, and 🟪 gamma radiation

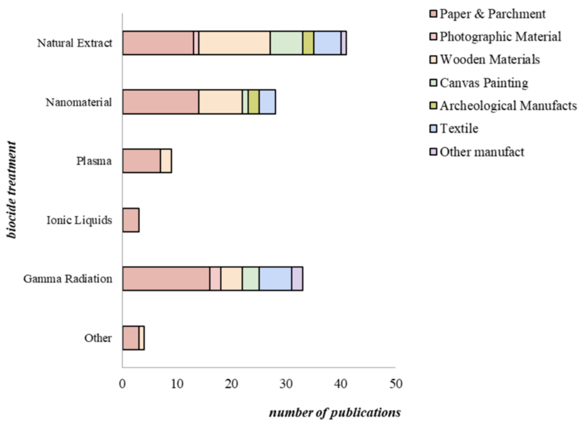

Fig. 2 Number of scientific papers divided per biocidal treatment and categorized per organic-media support typology

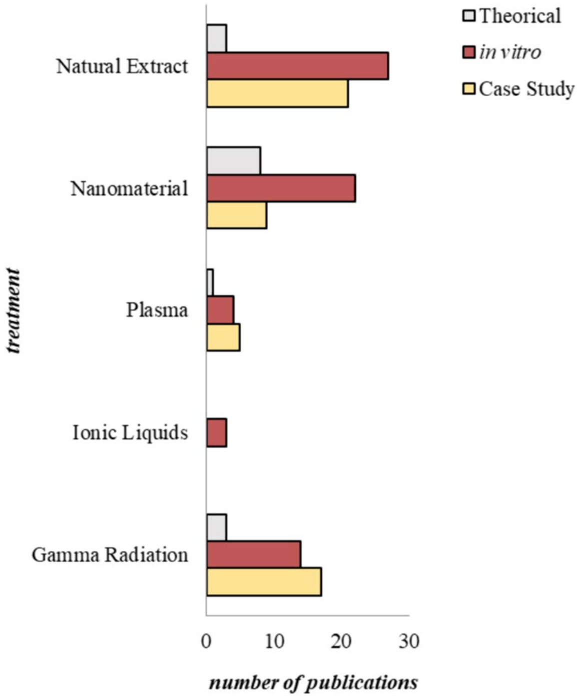

Fig. 3 Number of scientific papers divided per: in vitro studies (on mocks-up and Petri plates), Theoretical studies (literature reviews), and Case Studies (on real artworks)

also have very limited bulk, and their treatment may be more manageable for experimental purposes. More complex polymeric objects, such as paintings and contemporary art manufacts, pose a more ambitious challenge considering the heterogeneity of their constituent materials. For these types of artifacts there are no experimental research studies on the use of plasma or green solvents (ILs and DES), as is the case for organic archaeological findings.

Moreover, the majority of experiments reported in the literature are performed in vitro: the products and treatments have therefore been tested in *Petri* dishes (for antimicrobial assays) or simply on prepared mocks-up. However, there are in vivo experiments (case studies), especially regarding plant extracts and gamma radiation (Fig. 3).

In general, these data highlight that while research is rapidly progressing towards the discovery of new ecological and safe solutions, on the other hand, these are often biocidal treatments whose protocols still need to be explored and consolidated.

Biodeterioration of organic-media: the role of fungi and bacteria

Pathogenic organisms of artistic objects are responsible for damages of both chemical-physical and aesthetic nature and are favored by environmental conditions such as relative humidity, temperature, UV exposure, presence of CO_2 or environmental pollutants, as well as by the chemical and morphological characteristics of the substrate, such as porosity and surface roughness [10]. Biological micro-systems encompass a wide category of pathogens including bacteria, fungi, algae, and lichens [11], The latter two, however, predominantly affect inorganic-media artifacts and those exposed outdoors, such as stone monuments, mosaics, sculptures, frescoes, and murals [12], and will not be considered in this study. Regarding bacteria, autotrophic species are mainly responsible for the degradation of inorganic substrates, such as sulfur-oxidizing bacteria and hydrogen bacteria (chemolithotrophs, colonizers of stone substrates) [13], nitrifying bacteria [14] and iron bacteria, which play a decisive role in the degradation of metallic artifacts. Heterotrophic bacteria, on the other hand, colonize organic supports such as proteolytic and ammonifying bacteria (characterized by the action of proteases and peptidases capable of metabolizing animal proteins of binders and substrates); cellulolytic bacteria, which often do not limit themselves to the depolymerization of cellulose [15] but also break down other wood and paper components such as lignin, gums, tannins, waxes, and fats. There are also amylolytic and lipolytic bacteria that act through amylases and lipases on paint layers [16]. Fungi represent a significant source of degradation for artistic objects on organic substrates as they are mostly saprophytes, highly metabolically versatile, and adaptable to extreme environmental parameters of light, temperature and humidity. For this reason, they are widespread on artifacts preserved in very different environments such as homes, museums and ecclesiastical structures, as well as on those exposed outdoor. For both categories of microorganisms, two types of degradation are observed: the first is of a chemical-physical nature, as the depolymerization processes of supports and binders and the emission of metabolites by pathogens lead to a deterioration of the constituent materials. The breaking of cellulose chains composing paper, wood, and textiles results in a considerable weakening of the support, quantifiable by the Degree of Polymerization (DP).

The same occurs for animal- and plant-based binders and adhesives made of collagen and starch, which lead to a lack of adhesion or cohesion in paint materials. When extracellular proteolytic enzymes hydrolyze the peptide bonds of proteins composing supports such as silk, leather and parchment, irreversible structural damage occurs. In addition to enzymatic depolymerization reactions, another damage can be caused by the interaction of original materials with organic acids secreted as metabolic products (oxalate, acetate, succinate, etc.) which promote the oxidation of polymeric chains, catalyzing depolymerization processes. Other types of pigmented metabolites can cause further aesthetic damage, making it more difficult to read the work [17, 18]. For each support, biological damage manifests different macroscopic morphological characteristics (Fig. 4), as described below.

Wood

Among the most common causes of biological damage on wood, there are three types of degradation known as brown rot, white rot, and soft rot, attributed to the action of fungi. In the first case, cellulose and hemicelluloses are primarily degraded, leaving the characteristic dark coloration of lignin; in the second case, the opposite phenomenon occurs, as fungi feed on lignin leaving the wood devoid of its dark pigmentation. Soft rot generally affects the most superficial layer of wood, causing a significant loss of material [19] Additionally, chromatic alterations caused by chromogenic fungi producing pigmented metabolites can be observed, such as *reddening* (typical in conifers and produced by many species of Basidiomycetes), *bluing* (frequent in pine species by Ascomycetes), and *greying* (found in beech, mainly the work of Ascomycetes) [16]. Bacteria cause a slower degradation compared to fungal action and are responsible for phenomena such as erosion, cavitation, and perforation; however, they are very active in submerged or impregnated woods. A

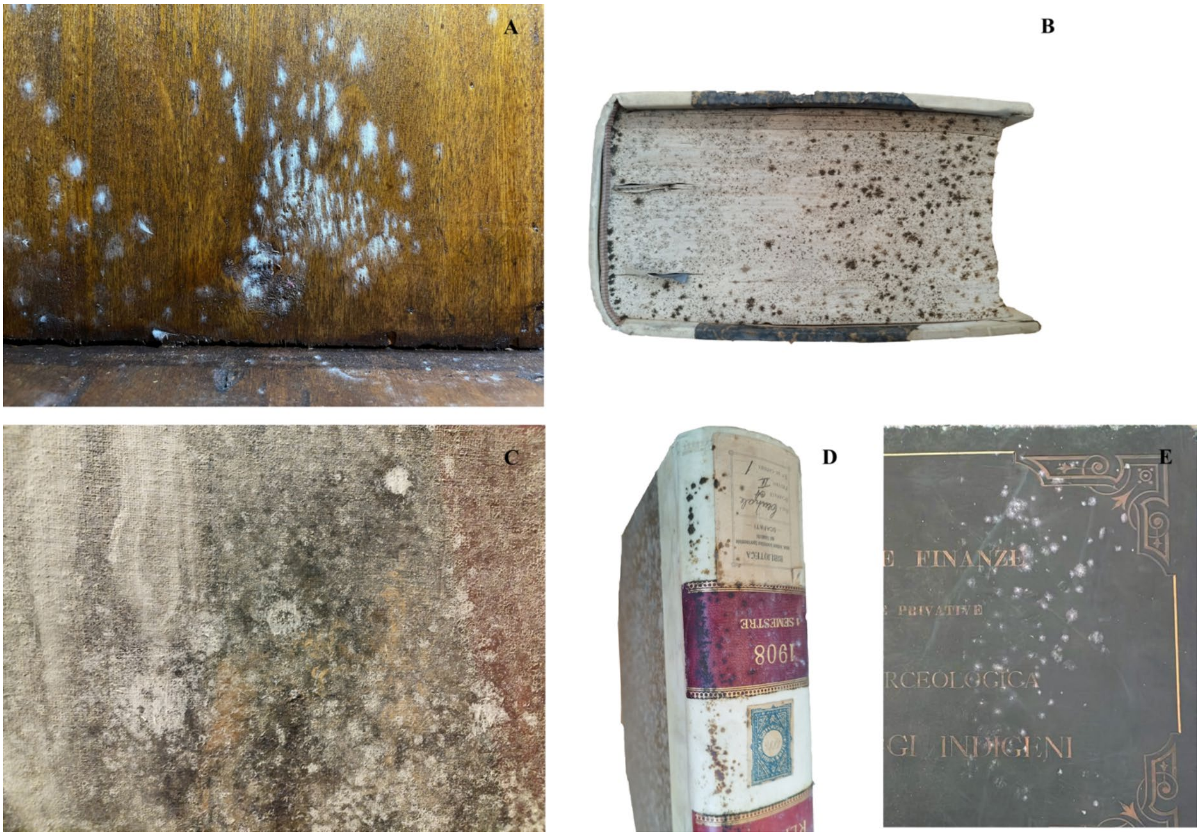

Fig.4 Fungal Colonization on: **A** Wooden Furniture; **B** Paper book; **C** Canvas Painting (*recto*) **D** Leather book's cover; **E** Linen book's cover

parameter that plays a determining role in resistance to biological degradation is the chemical composition of the wood, specifically the amount of contained moisture and the percentage of lignin and trace substances such as resins, fats, and oils. The latter makes wood less "appetizing" to most organisms and insects, as demonstrated by the classification based on "durability" in the UNI EN 350–2 2016 standard. The classification refers to the "Natural durability of the main European wood species used in construction against different xylophagous organisms", distinguishing between sapwood (outer and lighter crown, less durable) and heartwood (darker inner area due to higher lignification, more durable) [20].

Paper

Paper derives from a manufacturing process that involved the use of wood pulp or textile fibers, although production processes and bleaching treatments have evolved considerably over time in terms of techniques and materials, up to the manufacturing of modern paper starting from the nineteenth century. Therefore, in addition to the presence of cellulose and lignin, there may also be glues based on animal gelatin or starch, mineral fillers, and bleaching agents [21]. One of the most widespread damages is "foxing" [22], a chromatic alteration presented as brown/reddish spots that coincide in most cases with the colonization of fungi from the families *Aspergillus spp.* and *Penicillium spp.* [23]. It results in the production of malic acid, glucose, cello-oligosaccharides, and γ-aminobutyric acid. It's suggested [24] that this foxing process involves the formation of melanoidins through the Maillard reaction. Specifically, cello-oligosaccharides and γ-aminobutyric acid, along with other amino acids produced by specific fungi, contribute to the creation of these melanoidins. This phenomenon is accompanied by the depolymerization of the support [25]. Similar macroscopic degradation occurs in audiovisual materials [26] as in the case of audio-visual tapes and photographic media: both the supports (cellulose nitrates, diacetates and triacetates and polyethene) and the photosensitive emulsions (based on organic binders such as gelatine, albumen and collodion) can be easily targeted by fungi [22].

Audio-visual materials

Audio-visual materials are often associated with paper-based materials from a conservation perspective. However, the composition of these supports varies significantly based on the type of artifacts, their dating, and the composition of industrial components, as well-documented in the literature [27]. Audio-visual materials emerged in the early nineteenth century and can be categorized into three main types of artifacts: exclusively auditory materials (such as tape and vinyl recordings), primarily visual materials (such as photographs and slides), and a third category that reflects the evolution of both, as seen in cinematographic films. These materials are also susceptible to foxing and other chromatic alterations [28, 29]. In the presence of humidity, as for previously described supports, microorganisms produce various organic acids such as acetic, lactic, fumaric, or citric acid which are responsible for the acidification and depolymerization processes of the substrates. Moreover, they produce enzymes—such as gelatinase—that play a key role in breaking down the animal-based emulsion layers, rendering the system vulnerable to relative humidity changes [30].

Some microorganisms can also bioaccumulate and chemically transform silver ions present in the emulsion layer and, as a consequence, this process suppresses the antimicrobial effect of silver ions, leading to faster biodeterioration [27].

Fabrics and canvas paintings

Fabrics can be of animal origin (such as silk and wool) or of plant origin (cotton, linen, jute, and hemp). In the first case, the materials are proteinaceous, highlighting the presence of keratin for wool, fibroin and sericin for silk, with other trace lipid substances. The degree of crystallinity, hygroscopicity, and purity of the fabric are determinants in defining the durability to biological degradation of these materials\. Both fungal and bacterial colonization can lead to enzymatic hydrolysis, resulting in the disintegration of animal fibers, thus causing a loss of physical–mechanical resistance, fragility, and chromatic alteration [31, 32].

Even for fabrics of plant origin, purity in the content of cellulose and hemicelluloses is an important factor in assessing the biological risk. In the specific case of painted canvases, they are composite artifacts where the *recto* and *verso* of the work present two substrates with different compositional and morphological characteristics. It is commonly believed that the *verso* of a painting is more exposed to biological risk due to the presence of more easily degradable materials, which, in addition to the canvas, are represented by glues based on gelatin, casein, starch, and eggs. On the *recto*, the presence of inert fillers in paint layers such as gypsum and kaolin, and pigments based on minerals, salts, and metal oxides, act as inhibitors of colonization [16]. However, a recent study demonstrates that for a painting displayed on a wall in an environment potentially rich in fungal spores, gravity plays a fundamental role, as it favors the deposition and adhesion of microorganisms to the paint film rather than to the back of the canvas. In a contaminated environment, indeed, the *verso* of a painting may be less exposed to direct contact with microbes and spores, and the diversity of microorganisms present on the surface is considerably lower [33].

Leather and parchment

The susceptibility to biological attack of these types of artifacts varies depending on the type of treatments and additives applied during processing phases, from skinning to tanning and drying [34, 35]. It also varies depending on the type of animal from which it is derived and its growth conditions[36]. Tanning processes can be carried out using products of vegetable origin, which are more easily degradable compared to other substances such as chromium[37]. Treatments with sea salt, tannins, and chromium were intended to limit the action of biodeteriogens; however, some mechanisms have been identified whereby biological attacks have been favored [38]. This is the case, for example, of salting with sodium chloride, to whose crystals haloalkaliphilic microbes (belonging to *archaea*) that proliferate in saline environments adhere, paving the way for colonization by heterotrophic organisms. A chain reaction is then triggered in which the colonizers of the first phase promote the formation of new colonizations. These supports present macroscopic degradation in the form of red or purple stains and chromatic alterations[39]; in the case of manuscripts, the margins of the pages, in contact with the outside, are the first areas to show physico-chemical damage caused by the direct action of microorganisms but also by the corrosion of organic acids produced by them.

Plastics and synthetic polymers

A last and complex category of artistic supports is represented by polymeric artifacts of contemporary art, where there are objects of organic synthesis based on plastics with different formulations that have rapidly changed over the course of the industrial development of the last century. Today, these materials constitute not only the material of the artworks but also the material for restoration and intervention, as is the case with adhesives, consolidants, resins, foams, and polymer-based paints such as acrylics, vinyls, styrenes, urethanes, amides, propylenics, etc. Among vinyl polymers, common uses include polyethylene, polyethylene glycols (PEG), polyvinyl chloride (PVC), polypropylene (PP), polyvinyl acetate (PVA), and polystyrene, which can be subject to biodeterioration by fungi and bacteria such as *Aspergillus spp.*, *Mucor spp.*, and *Pseudomonas spp.* [40, 41]. The degradation of polymers occurs in two phases, in the first, the bonds with the lateral groups are cleaved, and subsequently the C–C polymer chain bonds are broken. Regarding petroleum-based polymers (PET, PE, etc.), they are generally more resistant due to the presence of aromatic hydrocarbons [42]. Similarly, other non-vinyl polymers such as polyurethanes, polyamides, and polystyrenes, and cellulose derivatives such as acetates, nitrates, and cellulose ethers, can be subject to degradation. Damages are often recognizable macroscopically in the form of discoloration, cracking, detachment, but also at the microscopic level as demonstrated by images from scanning electron microscopy (SEM) in some case studies. Although many restoration product formulations include preservatives, many of them, especially those water-based, tend to modify the bio-receptivity of the substrate [43].

Incidence of micro-organisms genera

Analyzing the information contained in the collection of articles assembled for this study, it was possible to identify the species of microorganisms, specifically fungi and bacteria, most frequently isolated from organic substrates and consequently most tested for the mentioned biocidal protocols.

Based on consulted literature, it is evident that the most commonly used fungal *genera* in experimental settings belong to *Aspergillus spp.* and *Penicillium ssp.* (references cited in the table) (Table 2). Specifically, the *Aspergillus spp.* genus is tested for eco-sustainable biocidal treatments in 30.47% of publications from 2000 to the present, while *Penicillium ssp.* is present in 18.90% of cases. Regarding bacteria, species belonging to the *Bacillus spp.* genus were tested in 28.12% of publications, while *Staphylococcus spp.* were tested in 15.62% of cases. Fungal species belonging to *Aspergillus spp.* are by far the most commonly isolated: they are considered a family of environmental pathogens, highly adaptable to different climatic conditions, and also very resistant in extreme conditions (heat, cold, drought). Both operators and artworks are constantly exposed to contact with the spores of these environmental microorganisms, so it is worth investigating what factors activate colonization mechanisms. Firstly, *Aspergillus spp.* can produce different types of extracellular enzymes such as cellulase, amylase, protease, ligninase, chitinase, pectinase: these are able to hydrolyze (or catalyze the process) most artistic substrates of organic origin. These processes are generally favored by the presence of high humidity [44].

It should also be noted that *Aspergillus spp.,* including the very common *A. fumigatus*, *A. niger*, and *A. terreus* often isolated from artworks, can potentially cause infections in humans as they are carriers of aspergillosis. While it is impossible to completely avoid contact with these species due to their environmental prevalence,

Table 2 Occurrence of micro-organisms per *genus* isolated on different organic-media artistic supports

Support typology	Fungi genera	Occ	Bacteria genera	Occ	References
Wood	*Aspergillus spp.*	10	*Bacillus spp.*	4	
	Penicillium spp.	5	*Streptococcus spp.*	1	[49–59]
	Trichoderma spp.	2	*Arthrobacter spp.*	1	
	Lecanicillium spp.	1	*Staphylococcus spp.*	1	
	Schyzophillum spp.	1	*Sphingomonas spp.*	1	
	Coprinellus spp.	1			
	Cladosporium spp.	1			
	Chaetomium spp.	2			
	Purpureocillium spp.	1			
	Fusarium spp.	1			
	Mucor spp.	1			
	Alternaria spp.	1			
	Rhizopus spp.	2			
	Streptomyces spp.	1			
	Trametes spp.	1			
	Pycnoporus	1			
Paper	*Aspergillus spp.*	13	*Bacillus spp.*	2	[60–73]
	Penicillium spp.	11	*Staphylococcus spp.*	2	
	Cladosporium spp.	9	*Myxotrichum spp.*	1	
	Chaetomium spp.	4	*Escherichia spp.*	1	
	Fusarium spp.	4	*Kocuria spp.*	1	
	Alternaria spp.	4	*Salmonella spp.*	1	
	Botrytis spp.	1	*Proteus spp.*	1	
	Chromelosporium spp.	1	*Pseudomonas spp.*	1	
	Epicoccum spp.	1	*Microbacterium spp.*	1	
	Phlebiopsys spp.	1			
	Toxicocladosporium spp.	1			
	Stachybotrys spp.	1			
	Athelia spp.	1			
	Aureobasidium spp.	1			
	Byssochlamys spp.	1			
	Talaromyces spp.	1			
	Rhodotorula spp.	1			
	Staphylococcus spp.	1			
	Myxotrichum spp.	1			
	Scopulariopsis spp.	1			
	Trichoderma spp.	2			
	Acremonium spp.	1			
	Trichosporon spp.	1			
Plant-based textiles	*Aspergillus spp.*	2	*Bacillus spp.*	1	[74–76]
	Penicillium spp.	1	*Arthrobacter spp.*	1	
Animal-based support	*Aspergillus spp.*	4	*Georgenia spp.*	1	[63, 71, 76–81]
	Penicillium spp.	3	*Bacillus spp.*	1	
	Trichoderma spp.	1	*Staphylococcus spp.*	1	
	Paecilomyces spp.	1	*Ornthinibacillus spp.*	1	
	Streptomyces spp.	1			
	Epiconum spp.	1			

Table 2 (continued)

Support typology	Fungi genera	Occ	Bacteria genera	Occ	References
Pictorial layer	*Aspergillus spp.*	2	*Escherichia coli spp.*	1	[50, 82–86]
	Cladosporium spp.	1	*Salmonella spp.*	1	
	Neocamarosporium spp.	1	*Eterococcus spp.*	1	
	Rizophus spp.	1	*Pseudomonas spp.*	1	
	Candida spp.	1	*Azotobacter spp.*	1	
			Serratia mar spp.	1	
			Staphylococcus spp.	1	
			Streptomyces spp.	1	
			Bacillus spp.	1	

working in areas where these pathogens are actively colonizing increases the risk of infection [45, 46]. It is therefore a genus towards which there is great interest and it is also the most isolated from painting layers in other literature reviews [47, 48].

From an ecological point of view, it is interesting to note that, while for fungi the isolation of some *phyla* compared to others is selectively determined by the type of substrate from which they are isolated, in the case of bacteria, the incidence seems to be more closely linked to climatic patterns, and therefore determined not by the substrate in question but by environmental factors [87]. In fact, it is evident that for fungi, mostly saprophytic organisms, are associated with the presence of Basidiomycetes, Agaricomycetes, Eurotiomycetes, and Sordariomycetes. In the case of bacteria, however, the distribution of the microbiome ignores the functional aspect but is rather determined by geo-climatic factors.

Safety and ecotoxicity of current commercial biocides

The available options on the market to counteract the biodegradation of artistic artifacts are not numerous, as already emphasized in previous studies [46, 88], and among these, even fewer are the formulations and active compounds designed for the treatment of organic supports: generally, these are mixtures based on quaternary ammonium salts (QACs), isothiazolinones and carbamates (CBs) (Table 3).

Quaternary ammonium salts have become commonly used due to their affordability and ease of dilution in water, allowing them to be employed not only as biocides but also as preservatives in adhesives and other preparations for art restoration. They are sold in mixtures or in purity at different concentrations, such as in the case of benzalkonium chloride (BAC). QACs are cationic surfactants, and their effectiveness is linked to their micellar

Table 3 Main commercial products for biocidal treatment on organic supports

Commercial name	Active compounds	Solubility	Action spectrum
Rocima 103®	Concentrated octylisothiazolone in a mixture of quaternary ammonium compounds	Water and polar organic solvents	Fungi, algae
Rocima 110®	Quaternary ammonium compound and tributyltin naphthenate	Water and polar organic solvents	Fungi, algae
DES-NOVO®	10% solution of benzalkonium chloride	Water	Molds, yeasts
Preventol RI50®	Based on dodecyl-dimethyl -dichlorobenzyl -ammonium chloride	Alcohols, ketones, chlorinated hydrocarbons, water	Fungi, algae, bacteria
Preventol RI80®	Based on alkyl dimethyl benzyl ammonium chloride	alcohols, ketones, chlorinated hydrocarbons, water	Bacteria, molds, algae, lichens
Biotin R®	Mixture based on dioctylisothiazolone, carbamate, and terbutrine	Apolar organic solvents	Bacteria, fungi, algae
Biotin T®	Mixture based on octylisothiazolone and quaternary ammonium salt	Water, esters, alcohols, and aromatic hydrocarbons	Bacteria, lichens, fungi, algae
SINOCTAN PS®	Based on 4,5-dichloro-2-octyl-isothiazolone and 3-iodo-2-propynyl *N*-butylcarbamate	Apolar hydrocarbons	Algae, mosses, lichens, yeasts, fungi, molds, bacteria

structure which enables them to act on the cell membrane of microorganisms by affinity with phospholipids, altering their osmoregulatory and physiological functions [89]. The literature presents conflicting results regarding the safety of such products, which vary depending on the methods of use, frequency, and concentrations employed. However, risks to respiratory pathways have been highlighted due to the volatility of ammonia, as well as potential irritations and allergies from direct contact with skin and mucous membranes [90]. As previously mentioned, the extensive use of these substances in various industrial, domestic, agricultural, food-related sectors, etc., is laying the groundwork for the generation of biotic resistance, leading to an increase in antibiotic tolerance by many microorganisms. Lastly, considerations must be made regarding reports of eco-toxicity: while increasing the length of the alkyl chain enhances the antimicrobial efficacy of such cationic surfactants, it decreases their biodegradability and increases the risks associated with eco-toxicity [91–93].

Regarding products based on isothiazolinones, which have the molecular formula $(CH)_2SN(H)CO$, mainly two types of compounds are recognized: octylisothiazolone (OIT) and dichlorocthylisothiazolinone (DCOIT). These compounds act on the cell membrane for bacteria and on the cell wall for fungi, thanks to the action of the S and N atoms present in the heterocyclic structures of the molecule, which interfere with the enzymatic activities of the cells. In this case as well, recent reports have emerged regarding the safety of these substances, derived from both inhalation and direct contact with the skin [94].

Finally, carbamates are often present in the mentioned mixtures: these are organic compounds consisting of an amino group linked to an ester group, with molecular formula $-NH(CO)O-$, and they are generally used as pesticides for their insecticidal properties. The mechanism of action of such compounds lies in the inhibition of acetylcholinesterase (AChE), the enzyme responsible for breaking down acetylcholine (ACh), a neurotransmitter in the central nervous system of insects, rodents, and even humans. According to this principle, there is a high risk for humans exposed to these substances both through skin contact and inhalation [95, 96].

These products are generally used for direct application on the surfaces to be treated, either by spraying or brushing, and caution is required by the operator who must be equipped with personal protective equipment (PPE). However, it should be remembered that these substances remain within the treated supports, and are intended to be reapplied periodically as a preventive maintenance treatment. This aspect emphasizes the frequent and intensive use of these products, which may lead to an accumulation of potentially toxic substances for the operators that have to be in contact with the substrates of treated artworks.

Moreover, from the cited literature, it is evident that the eco-toxicity risk associated with the use of such products may significantly affect marine and terrestrial ecosystems, although there is less available data for the latter. The mentioned compounds readily biodegrade aerobically, but their dispersion in the environment does not follow the same pattern; instead, they gradually sediment over time [82]. This phenomenon can occur, for instance, with outdoor-treated artworks or with treatments' discharge residues into wastewater.

Green biocides

Plant extracts

Trials using plant-derived extracts are among the most conducted for the search of green alternatives for the biocidal treatment of artistic objects. Scientific papers mainly focus on the use of essential oils, whose biocidal efficacy has already been extensively documented in in vitro studies [97–100]. Among these, the properties of oils extracted from plants belonging to *Lamiaceae* family stand out, since they result being particularly rich in bioactive aromatic compounds. Even in applied studies for cultural heritage conservation treatments, oils derived from *Lamiaceae* are the most tested, such as lavender, mint, basil, oregano, marjoram, rosemary, thyme, and sage species [49–52, 60–62, 74, 75, 77, 78, 82, 101–112].

Specifically, the anti-fungal and anti-bacterial properties depend on the concentration and type of secondary metabolites present in the extracts belonging to compound classes such as terpenes, fatty acids, aromatic organic acids, phenols, and alkaloids. These substances are produced as a defense mechanism against insects, fungi, and bacteria and for this reason, the same mechanisms of action can be triggered by extracting essential oils rich in bio-actives and using them on active biological colonization. They may act on multiple levels: the lipophilic components interact with the cytoplasmic membrane of microorganisms, causing morphological and physiological alterations of the cells, and also interrupt the function of the proton pump, causing a modification of the intracellular pH [113]. These processes result in the inhibition of the metabolic activity of microorganisms and can lead to their death [98]. In general, the fungicidal mechanisms of the mentioned compounds can act either on the membrane/cell wall or within them. In the first case, the interaction of the biocidal agent targets a sterol, the ergosterol, present in the cell wall of fungi and ensuring its integrity. Its neutralization, or inhibition of the sterol biosynthesis process, causes osmotic and metabolic instability of the cell, ultimately compromising its activity [114]. The same occurs if there is a blockade in the production of β-glucans, thus inhibiting the formation of the cell wall. In the second case, for processes acting within the cell, multiple mechanisms can occur. Some oils disrupt the mitochondrial electron transport chain, thereby altering the membrane potential, or inhibit the proton pump, consequently reducing ATP production and the cell's respiratory process, leading to its death [98]. Interaction with essential oils can also promote the production of reactive oxygen species (ROS), responsible for oxidative damage within the cell. An extracellular mechanism interferes with cell-to-cell communication (quorum sensing), the ability to interact with exogenous factors and exchange information: when compromised, biofilm formation can be inhibited [115].

The results of the cited studies show inconsistent responses from individual essential oils towards the same bio-deteriogen *genera*, attributable to the different concentration of bio-active substances and the relative sensitivity of microorganisms to each of them.

For example, phenolic compounds such as carvacrol, eugenol, or thymol are active against both Gram-positive and Gram-negative bacteria due to the presence of hydroxyl groups that cause protein denaturation. A factor that enhances the antibacterial action of terpenoids is instead the presence of carbonyl groups. The antibacterial effectiveness depends not only on the presence of reactive functional groups -OH and $C=O$ but also on the stereochemical features of the molecules [116].

For antifungal properties as well, there are some more functional classes of molecules, as in the case of phenols, which demonstrate greater effectiveness in the presence of alkyl groups in the benzene ring of the phenol due to increased steric hindrance [117]. In general, the classes of molecules demonstrate effectiveness in inhibiting growth in the following order: phenols, cinnamic aldehydes, alcohols, aldehydes, ketones, ethers, and finally hydrocarbons [118].

The bactericidal/bacteriostatic, fungicidal/fungistatic activity significantly varies for each substance towards individual families and species of bio-deteriogens, resulting in a highly variable efficacy range depending on the type of biological colonization. Due to the selective effectiveness of each oil, research indicates that blends of essential oils have a greater biocidal power compared to the individual oils that compose them [119]: it should be considered that biological degradation results from a combined and synergistic action of multiple pathogenic microorganisms, thus requiring a diversified action of multiple bio-active substances to eradicate them. Furthermore, in most of the cases consulted biocidal effectiveness appears to have a dose-dependent trend.

However, a critical aspect not properly addressed in the cited literature is connected to essential oil extraction, since brings with it some sustainability-related challenges both in terms of yield quantity and extraction processes. Regarding the former aspect, the low extraction yields typically associated with these substances is significant. Also, the chemical and physical processes employed for extraction often still involve the use of organic solvents, making the process environmentally unfriendly.

The application protocol for essential oils and pure bioactive compounds requires careful consideration, especially when it comes to direct application on artistic media. To obtain a homogeneous mixture to be applied by spray or brush on the entire surface it may be necessary to emulsify the compounds which, however, requires the use of surfactants or organic solvents. In both cases complications may arise from interactions with the materials of the artwork (as in the case of ground layers and pictorial films). Not to mention the strong fragrance that could remain on the surface of the object even after the end of the restoration process. The most suitable method of application for the restoration of cultural heritage would suggest instead the use of such substances by fumigation with no direct contact: exposing the surface to volatile components has been a successful intervention in many of the mentioned studies [50, 63, 64, 77, 82, 103, 107]. Must be considered, however, the aspects related to timings of restoration works, which may not coincide with an extended treatment in a modified atmosphere chamber.

Last, it is worth noting that other types of plant extracts are unfortunately underexplored in the field of cultural heritage. Indeed, the literature suggests numerous alternatives of extracts derived from medicinal plants or agri-food waste with potentially significant antimicrobial activity [120–123], which should be considered in a circular economy perspective for the valorization and reuse of waste materials.

Nano-materials

The use of nano-structured biocides is widely spread for the application to cultural heritage. The nature of such formulations can vary considerably and the category encompasses various types of nanoparticles and/or encapsulations with different core materials and matrices depending on the required characteristics for the application. Two macro-categories can be distinguished based on the nature of the active ingredients: organic or inorganic. In the former case, there are some formulations based on essential oils and bioactive molecules of plant origin already mentioned in the literature [63, 64, 124–126]. The substances used are structured in the form of nano-emulsions or encapsulated in polymeric matrices. Overall studies dedicated to this type of nanomaterials that involve the use of pure molecules such as carvacrol, thymol, eugenol, or essential oils present the same issues previously mentioned regarding the chemical instability of these compounds and also variable antimicrobial performance. Last, it has been highlighted that organic-based biocide are less efficient and their effects tend to be less enduring over time than the inorganic ones [127].

When the active ingredients are inorganic, they are generally represented by metallic oxides such as TiO_2, ZnO, MgO, and metals like Ag, Cu (MNPs). The applications of such products have been extensively studied for artifacts of inorganic origin, particularly for stone restoration for sites and monuments [127]. However, experiments also include paper materials [65, 66, 83, 128–131], wooden supports [65, 130, 132–135], painting layers [124], textiles [136] and archeological manufacts [76, 79, 137].

The use of MNPs is generally multifunctional, as their targets often include not only the inhibition or disinfection of microorganisms but also the de-acidification of the substrate, as well as the consolidation and improvement of the physical and mechanical properties of the treated supports [138]. Based on the different synthesis methodology, can vary significantly in size within a range of approximately 4 nm-400 nm; and based on this aspect, the antimicrobial efficacy can also vary.

In general, the action mechanisms of metallic nanoparticles are manifold and yet not fully understood: indeed, as highlighted in previous studies [139], they can interact at the membrane potential level, creating an electrostatic interaction between the positively charged MNPs and negatively charged cell membranes. This interaction has the potential to trigger conformational alterations in membrane phospholipases stimulating phospholipid hydrolysis, the generation of reactive oxygen species (ROS), and lipid peroxidation, ultimately resulting in pore formation [139].

Titanium dioxide (TiO_2) is one of the most widely used nanomolecules among those mentioned, and its principle of operation is linked to photocatalytic action: a semiconductor material generates reactive oxygen species (ROS) when exposed to UV light or solar radiation. ROS originate from molecules found in the atmosphere (O_2 and H_2O), encompassing superoxide anion radicals (O_2), hydroxide radicals (OH), and hydrogen peroxide (H_2O_2). These species possess the ability to eliminate microorganisms through oxidative damage to their cell membranes [140]. This nanoparticle has been employed alone or conjugated with other molecules, not only as a biocidal solution [141] but also suspended in hydrogels [128], added to an antimicrobial consolidant [134] or coatings [79]. Although experiments report different MICs (Minimum Inhibitory Concentrations) depending on the microorganisms tested due to the characteristic species-specific behavior, TiO_2 shows pronounced activity starting from about 0.1 mg/ml [127].

Zinc oxide has the same mechanism of action and cost-effectiveness as titanium dioxide, offering similar antifungal and antibacterial efficacy. Additionally, zinc oxide exhibits antimicrobial activity even in the absence of light. In this case, many studies report the use of nanoparticles as additives within coatings [83, 130, 142], adhesives [130] and consolidants [134].

Magnesium oxide proves to be a multifunctional nanoparticle as it not only acts on an antimicrobial level (active concentrations starting from 1 mg/mL) but also serves as an acid-neutralizing agent for cellulose-based textiles and paper [131]. Studies report the antibacterial efficacy due to the induction of oxidative stress and intracellular content leakage caused by cell membrane disruption [129].

Regarding Ag NPs, they are also among the most widely used for application in cultural heritage with high effectiveness (starting from the range of 0.04–0.06 mg/mL). In terms of their mode of operation, research indicates that silver nanoparticles (Ag NPs) tend to gather on both the cell wall and membrane, resulting in cytoplasmic shrinkage and membrane disruption. Moreover, Ag NPs have the capability to attach to membrane proteins, consequently impacting membrane permeability, the respiratory chain, and ion transport. Under specific circumstances, Ag NPs may penetrate the cell, where they interact with DNA and/or intracellular proteins, thereby disrupting processes such as transcription, translation, and sugar metabolism [64, 132, 133, 143, 144].

Generally, nanomaterials have attracted significant interest, especially due to the potential utilization of commercially accessible MNPs, which likely contributed to the upsurge of experimental trials. It should be noted that the processes of biosynthesis of nano-metals are also increasingly sought after. This allows not only to obtain an antimicrobial solution without risks related to eco-toxicity and human safety, but also eco-compatible from the perspective of its production [79, 145].

Future perspectives: other chemical approaches

A small portion of the literature is dedicated to other biocidal treatments with chemical action, which represent a minority especially when considering their sole application to artifacts on organic support, yet they represent a promising perspective. Among these, the use of Ionic Liquids (ILs) certainly stands out, which are liquid-state salts composed of an organic cation paired with an organic or inorganic anion.

The potential of ILs stems from the ability to customize mixtures based on the application and desired characteristics: the 10^{18} possible combinations of salts indeed offer a wide range of usage and effectiveness that should be further investigated.

Studies on the use of ILs as biocides are not extensive, but there are some applied studies on paper artifacts that show positive results on antifungal and antibacterial activity. The biocidal mechanism of action of Ionic Liquids lies in the interaction with the cell membrane: specifically, the hydrophobic and lipophilic nature of the alkyl chains increases affinity with the phospholipid layer of the cell membrane, penetrating it and inhibiting the growth of microorganisms. According to the literature [146–148] it emerges that increasing the length of the alkyl chain and the apolar nature of the mixture enhances its antimicrobial properties. Research indicates that the cations found in ILs have the ability to permeate the plasma membrane, resulting in increased uptake within the intracellular matrix, thereby influencing organelle function. Furthermore, these charged cations have the potential to bind to receptors on the plasma membrane, disrupting the normal transport of ions and molecules necessary for cellular processes [149].

An innovative and still unexplored method is represented by treatment using supercritical CO_2, where the critical state threshold of carbon dioxide is exploited to decontaminate a paper substrate subject of the case study [150]. However, this treatment requires sophisticated and not easily accessible equipment, and above all presents logistical difficulties for execution, considering that in the mentioned research the case study was sectioned to be inserted into the extraction chamber, leading to the destruction of the substrate. The inhibition mechanisms involved in the process are not well understood, but sudden pressure changes and expansion of CO_2 within the cell membrane, as well as significant pH variations, are suggested as determining factors.

New studies are also focusing on the use of Deep Eutectic Solvents (DES) for biocidal treatment as well as surface cleaning [4]. In this case as well, the few existing studies refer to their application on stone artifacts [151] achieving good antimicrobial performance. The tested mixtures are based on choline chloride, in combination with oxalic acid, malonic acid, glycerol and urea which, when mixed in aqueous solution, reach rather low pH values to be safely used on surfaces of artistic artifacts (pH 2.8–7.2). To consider the possibility of applying DES to organic support materials the pH criticality should be addressed as well as practical application aspects due to their viscosity.

Among the options mentioned in this section, ionic liquids represent the most promising option in terms of antimicrobial performance as well as practical feasibility since they can be easily applied by spray or brush on the surface to be treated.

Physical treatments

Plasma

Plasma stands out as a promising preservation treatment to counteract bio-degradation. This technique involves the use of plasma, a partially ionized gas but electrically neutral in which its electron temperature ranges in the thousands of Kelvin, while the temperature of neutral species and ions remains close to environmental values. Plasma, as a state of matter, is induced in a gas by creating an electromagnetic field between two electrodes, but there are many types of plasma that differ based on the gas pressure, its temperature, the power source, and the degree of ionization.

Non-thermal plasma, also known as cold plasma, garners particular attention being suitable for treating heat-sensitive materials: in the use of low-temperature plasma, a distinction is made between low-pressure or vacuum plasma, and atmospheric pressure plasma, which allows for treatment in open spaces. Plasma presents a wide array of applications on organic-media heritage: cleaning and removal of non-original layers, de-acidification of supports and polymerization of cellulosic substrates thanks to the cross-linking processes [152–154]. This type of treatment has been primarily tested on paper substrates, demonstrating a 100% biocidal action with plasma exposure ranging from 5 to 15 min [155]. The inhibitory and biocidal behavior shows species-specific trend and a direct proportional correlation between exposure time and antimicrobial effectiveness [67–69, 156]. In fact, not all studies demonstrate fungicidal activity, but rather an inhibitory activity [157], with some significant pre/post-treatment modifications regarding surface pH and color [67]; overall, there is always an improvement in the mechanical properties of paper supports [125, 126] while no difference in mechanical resistance has been detected for cellulose-based fabrics [53].

Depending on the chosen ionized gas (O_2, He, Ar, Ne, Xe), different action mechanisms may be involved for micro-organism inactivation: oxidative damage, DNA deterioration, cell wall disruption or cell membrane permeabilization.

Overall, the technique shows promising results, but the majority of research has been concentrated only in the last 10 years. Therefore, it would be necessary to further investigate the logistical aspects of the treatment and evaluate its application to different types of supports.

Gamma radiation

Gamma radiation is an electromagnetic radiation emitted by an unstable nucleus of an atom during radioactive decay and it has been used as a safe sterilization method in the medical and food sectors for decades.

The use of gamma radiation for the decontamination of cultural heritage has been experimentally spreading since the 80 s, as evidenced by experiences documented in the literature [54, 158–160]. The enduring interest demonstrated over decades, which still attracts research attention, proves the potential of such treatment: the high effectiveness of this technique is due to the action that radiation has on the DNA of microorganisms, generating free radicals that interfere with the bonds within the double helix. Despite this, there are reports in the literature of some cases of radio-resistance. The primary factor determining an organism's resistance to gamma radiation is its ability to mend single strand breaks as a result of the activity of its DNA repair enzymes, as consequence strains that lack this skill are far more radio-sensitive than the rest. For instance, yeasts withstand radiation better than molds; and greater resistance in Gram-positive compared to Gram-negative bacteria highlights the relevance of peptidoglycan in bacterial resistance against the deleterious effects of gamma rays [161].

Free radicals, characterized by their extremely unstable and energetic nature with a short lifespan of 10^{-3} s, also contribute to long-term post-irradiation effects. These effects primarily occur through the indirect action of radiation-induced free radicals, with oxygen present in the air during irradiation playing a crucial role in oxidative degradation. Since this degradation process is closely linked to the diffusion rate of oxygen within the material, it becomes apparent that, for the same absorbed dose, the longer the exposure time at a low dose rate, the more significant the resulting damages. However, given that the production of free radicals is directly proportional to the radiation dose, it is feasible to minimize oxygen degradation by operating at the highest possible dose rate (while still compatible with the treated material) [158].

The radiation dose to be applied for treatment varies depending on the characteristics of the support's typology; however, in established protocols, it is suggested not to exceed 10 kGy to preserve the chemical and physical features of the support structurally and colorimetrically [159]. In the case studies reported in the literature, however, different ranges of radiation doses have been applied. For example, pictorial films on panel and canvas supports have been treated with higher ranges (25–33 kGy) without reporting alterations in the substrate of the artwork [162–164]. Similarly, complex polymeric objects, such as in the case of ethnographic collections, artifacts have been treated with radiation doses up to 200 kGy [165, 166]. Paper and photographic artifacts are the most tested, and a radiation value lower than 10 kGy is recommended for effective and non-invasive treatment [70, 71, 80, 167–176]. In literature, the correlation between increasing radiation doses and their effect on the physico-chemical properties of paper has also been investigated, demonstrating that doses above 15 kGy decrease the degree of polymerization of cellulose (DP) and alter the colorimetric response of the substrate. However, for fungi recognized in the literature as more tenacious, a range of at least 15–25 kGy is recommended [70, 71]. As well as per plant- and animal-based tissues, recommended values range between 10–20 kGy [81, 167, 177, 178].

As for wooden supports, the doses experimented within literature are significantly higher, ranging between 20 and 200 kGy [55, 56, 179, 180]. These experiments demonstrate conflicting results regarding the effects of high doses of radiation on the physical–mechanical properties of wood, which are negatively influenced by irradiation, highlighting especially the risk of re-colonization over time.

Overall, the use of gamma radiation compared to other physical techniques such as plasma or UV radiations appears to be more established experimentally and better understood for the effects that the treatment has on various types of substrates. However, physical treatments remain to date an experimental niche as they require highly specific equipment and resources that are unlikely to fit into the working practices of conservators.

Conclusions

From the brief analysis of the commercial options available on the market, it emerges that the literature on QACs, carbamates, and isothiazolinones –based products has been focusing for years on the impact of these substances on marine ecosystems and soils, as well as on the development of bio-resistance by target microorganisms and their toxicity profile for humans. The cited literature clearly indicates the motivation behind the increasing research trends over the past twenty years, which have shifted toward finding alternative solutions that are safe for humans, bio-based, or have limited environmental impact.

The two reported macro-categories of intervention, respectively with a chemical and a physical approach, are imbalanced in bibliometric terms. This discrepancy can be attributed to the greater ease of reproduction and availability of materials used for the first typology. The physical approach, in fact, requires sophisticated instrumentation and highly specialized personnel, as is the case with gamma ray or plasma treatment. Additionally, it is impractical to experimentally reproduce physical treatments within restoration laboratories, especially in private or museum settings. Furthermore, these techniques currently have logistical limitations related to the size of the treated surface, as they are mostly suitable for two-dimensional small-sized objects. Consequently, physical treatments have primarily been applied to paper-based substrates, while data regarding other types of three-dimensional supports are lacking.

Chemical treatments, on the other hand, do not present the same difficulties related to the type of substrate and the size of the surface to treat, and they are generally more accessible in terms of feasibility and costs. This applies to natural extracts and organic/inorganic nano-structured materials, widely used on a variety of different artifacts. Despite the high-performing results, it's worth noting two aspects: first, the experimental protocols for assessing the antimicrobial properties are not standardized, making it difficult to compare the effectiveness of bioactive substances investigated in different studies. Some papers refer to the Minimum Inhibitory Concentration (MIC), while others focus on inhibitory concentrations (IC_{50}, IC_{90}) or on the biocidal action, resulting in different and not easily comparable outputs. The second critical aspect, which applies to all the techniques described in this study, is the lack of data regarding the treatment of contemporary art manufacts.

Contemporary art objects are problematic due to the heterogeneity of their constituent materials and the complexity of identifying all the synthetic polymers involved. These formulations can vary significantly and are sometimes protected by patents. The rheological studies on the interactions between bioactive substances and such materials present a complex challenge that the scientific community must address. Last, innovative proposals involving Deep Eutectic Solvents (DES) and Ionic Liquids (ILs) have recently been explored in the field of green chemistry for various industrial applications due to their sustainability and potentially high selectivity. However, these options remain relatively unexplored for their biocidal activity on artworks, necessitating further research to develop tailored mixtures specifically designed for this application.

Abbreviations

QACs	Quaternary ammonium compounds
ILs	Ionic liquids
DES	Deep eutectic solvents
NPs	Nanoparticles

Acknowledgements

Not applicable.

Authors contribution

B.P. data collection and writing; M.C.S. revision; S.P. conceptualization of the paper and revision. All authors read and approved the final manuscript.

Funding

Not applicable.

Availability of data and materials

No datasets were generated or analysed during the current study.

Declarations

Competing interests

The authors declare no competing interests.

Received: 21 June 2024 Accepted: 3 September 2024

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