Fungal Deterioration on Ancient Leather Artifacts

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Abstract

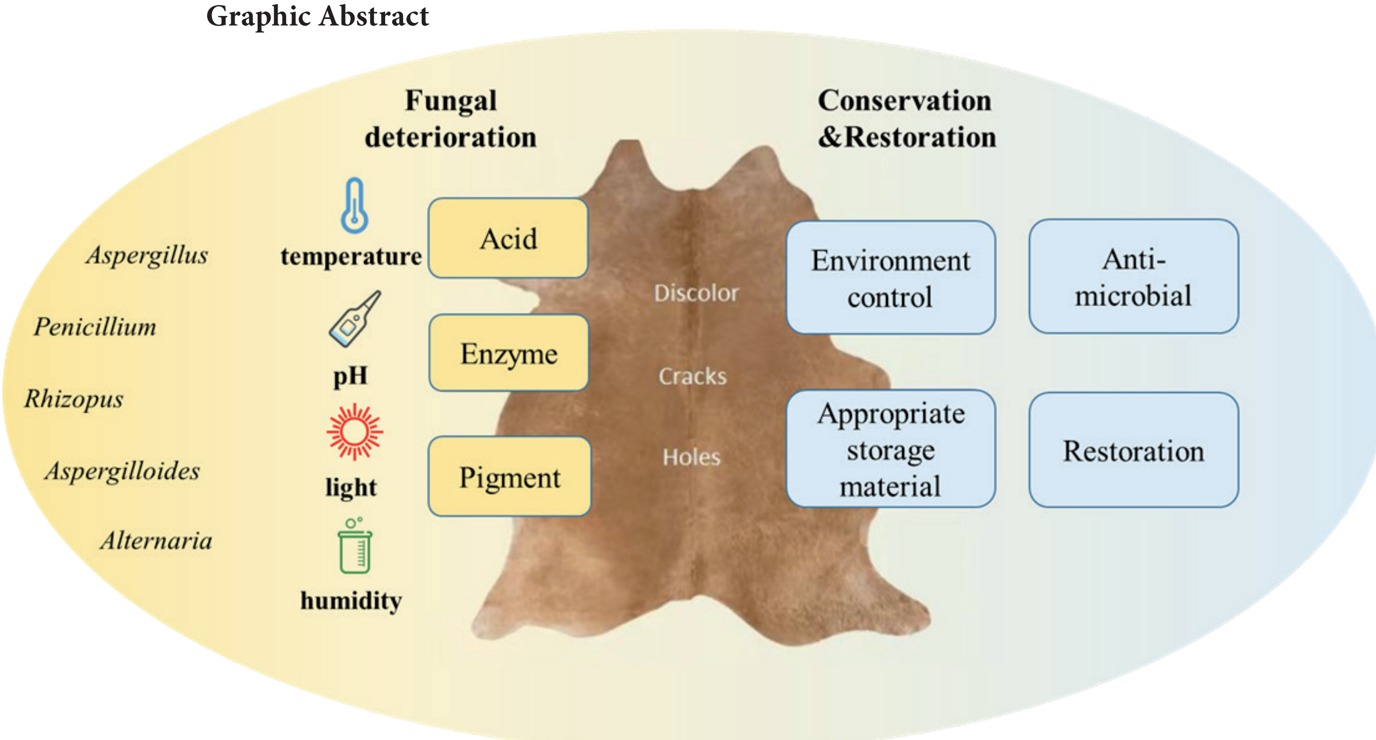
Fungal deterioration of ancient leather artifacts is a significant problem for museums and archives, as it might cause significant damage to the valuable cultural heritage. The growth of fungi on these artifacts is affected by such environmental factors as temperature, relative humidity, pH, and light exposure. The environmental factors that contribute to fungal growth and the impact fungi on the deterioration of ancient leather artifacts are discussed here. An overview is summarized on the strategies to prevent and control fungal deterioration, including the environmental control, the use of biocides, and conservation treatments, which is proposed to provide a valuable guidance for the preservation of ancient leather artifacts.

Introduction

Leather artifacts have played significant roles in human history, which might provide insight into ancient life with historical significance through its various uses, especially with evidence of their use dating back to the Neolithic period.[1] From clothing and footwear to bookbinding and upholstery, leather has been used for various purposes across different cultures and civilizations.[2]

However, over time, ancient leather artifacts can be susceptible to various forms of deterioration, including fungal decay, because of their high organic compound content and the suitable moisture, dark environment for fungal growth. In leather artifacts, there are organic compounds such as collagen, keratin, tannin, lipids, oils and others which are ideal sources of nutrition for fungal growth and proliferation.[2] Fungal deterioration of ancient leather artifacts is a complex issue that poses a significant challenge to

Graphic Abstract



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the preservation of ancient leather artifacts.[3] Fungal deterioration might cause the discoloration, weakening, structural integrity damage, and degradation of the ancient leather artifact, which changes the appearance and reduces their value in culture, history, science, etc.[4] Although there are fewer species of fungi on the substrate than bacteria, fungi tend to take more vital places for biodeterioration, because fungi can grow and reproduce even at lower temperatures and humidity levels than bacteria.[5] The growth of fungi on ancient leather artifacts is influenced by several environmental factors, including temperature, relative humidity, pH, light, and ventilation.[6] High levels of relative humidity and temperature provide ideal conditions for fungal growth and reproduction, while low levels of light and air flow might contribute to the development of anaerobic conditions, which could also promote the fungal growth.[7] The interaction of these environmental factors with the organic compounds in leather could create complex and variable conditions difficult to control and predict.[8] It is necessary to know the factors affecting the fungal growth and to develop strategies to prevent and control the deterioration for the preservation of these valuable ancient leather artifacts. The study of fungal deterioration on ancient leather artifacts is therefore of utmost importance.

This present review is aimed to provide an overview of the mechanism of fungal deterioration of ancient leather artifacts and the strategies used to prevent and control the biodeterioration by fungi.

Factors Affecting Fungal Growth

Fungi are diverse groups of microorganisms found in almost all environments, including museums and archives. They have been playing a crucial role in the decomposition of organic compounds and are responsible for the breakdown of dead plants and animal tissues. The availability of carbon sources, such as cellulose, collagen, oil, and starch are critical factors in determining the ability of fungi to colonize a substrate. However, for supporting fungi to thrive on a substrate, different conditions such as temperature, humidity, and water have to be met.[9,10] Therefore, how to design and control the environmental conditions, such as temperature and humidity, is crucial to inhibiting the growth and reproduction of fungi in order to prevent the damage to materials.

Temperature is critical for the growth and survival of fungi. Belli *et al.* tested the growth rate of *Aspergillus niger* under different temperatures by measuring the diameter of the colony every day and discovered that it grew quickly at the temperature between 30°C and 37°C.[11] Using the same techniques,[11] Plaza *et al.* discovered that *Penicillium* was able to germinate and grow between 4°C and 30°C, with the best growth at 25°C,[12] while Alwatban *et al.* found that *Cladosporium* grew quickly between 23°C and 25°C. Stevenson studied the germination behavior of *Eurotium halophilicum,* with the result that it could germinate between 20°C and 40°C, optimally at 30°C.[13] *Aspergillus*, *Penicillium, Cladosporium,* and *Eurotium* are four genera of fungi that are dominant on ancient leather artifacts, and their optimal temperature are summarized in Table I.

Relative humidity is particularly significant for fungal growth as well. Water might provide essential prerequisite for the growth and reproduction of fungi, as it could affect the amount of water available for the spore germination and growth of fungi.[16] Micheluz *et al.* found that in library bookshelves, a relatively closed environment would facilitate the germination of fungal spores due to the lack of ventilation and the condensation of water on the books during winter.[7] Additionally, vegetable-tanned leather is prone to fungal attack because of its more water-soluble

Table I

The optimal temperature of *Aspergillus, Penicilium, Eurotium and Cladosporium*.

Fungus	Found	Temperature	Reference
Aspergillus	Leather samples & air in the vicinity	30°C -37°C	5, 11
Penicillium	Air in the vicinity of leather samples	4°C-30°C, optimally at 25°C	5, 12
Eurotium	Leather samples	20°C-40°C, optimally at 30°C	5, 13
Cladosporium	Leather bindings	Optimally between 23°C-25°C	14, 15

nutrients for microorganisms, compared to the chrome-tanned leather. The latter is usually heavy oil and difficult to wet, making it less supportive of fungal growth. The ideal conditions for fungal growth include a relative humidity (RH) of 95-100% and a temperature (T) of 30°C, which is beneficial for the substantial fungal growth on the surface of the material.[10] Therefore, both guidance of Australian Institute for the Conservation of Cultural Material (AICCM) and American Institute for Conservation(AIC) recommend RH= 45%-55% and T= 15-25°C for preservation of ancient leather artifacts.[17] It is interesting to note that some xerophilic fungi, such as *Penicillium* and *Aspergillus halophilicus*, could still survive under relatively low temperatures (T= 23°C) and relative humidity (RH= 56.3%). In museum collection stage, the controlled temperature and humidity can be precisely maintained, while the fluctuations in these factors could still provide opportunities for the growth and reproduction of certain fungi, particularly for xerophilic fungi.[7]

The pH of the ancient leather artifacts and environment could affect the growth and reproduction of fungi as well. Most fungi could grow under a broad range of pH values, depending on the environment of germination and metabolic production of the fungi. Gock *et al.* studied the influence of pH on some xerophilic fungi (*Eurotium rubrum*, *E. repens*, *Wallemia sebi*, *Aspergillus penicillioides*, *Penicillium roqueforti*, *Chrysosporium xerophilum* and *Xeromyces bisporus*), and found that they could produce a range of acid by the anaerobic respiration of fungi. It was revealed that these fungi favored slightly acidic condition (pH=4.5-5.5) more than a neutral one,[16] making it easier for these fungi to settle on acidic materials like ancient leather artifacts. On the other hand, however, some early phase ammonia fungi (eg. *Amblyosporium*, *Peziza*, *Ascobolus*, *Tephrocybe*, *Coprinus*) favored the pH between 7 and 8, which was probably correlated to the soil pH where the fungi were sporulated.[18] Once buried in alkaline soil, leather artifacts might encounter these fungi.

Light is a key factor in the regulation of fungal metabolic pathways and is one of the many signals for fungi to perceive and interact with environment, thus affecting its behavior.[19] The structure in fungi responsible for the interaction of fungi with light is called photoreceptor, which is activated by light exposure and starts the signal pathway to arise the cellular response.[20] Among all the fungi studied, *Neurospora crassa* is the best known for deep investigation of the function of White Collar-1 (WC-1) and VIVID (VVD), which is the gene for the light sensing behavior.[20-22] Light might affect different aspects of fungal growth, including conidiation, germination, and pigment accumulation. Lee *et al.* found that when exposed to white, blue and red light, the activity of *Aspergillus oryzae* was greatly suppressed.[21] *Aspergillus fumigatus* was commonly found on ancient leather artifacts, while Fuller found that red and blue light had a strong negative effect on the germination kinetics,[23] as shown in Figure 1. Regarding the pigment accumulation, different fungi exhibit different behavior. Velmurugan studied five pigment-producing filamentous fungi and found that darkness might lead to the best pigment production,[24] which explained the reason why ancient leather artifacts buried deep under the soil still could not avoid discoloration. Fuller further proved that *Aspergillus fumigatus* could produce a lot more pigment in white or blue light than in the dark.[23]

Fungi on ancient leather artifacts

Fungi rely on the carbohydrates, fats, and proteins in ancient leather artifacts for metabolism and are commonly found in genera such as *Cladosporium*, *Rhizopus*, *Scopulariopsis*, *Aspergillus*, *Penicillium*, *Chaetomium, Candida, Alternaria, Phaeosphaeria* and *Eurotium*,[5,14,25] with the most abundant genera of *Aspergillus*,

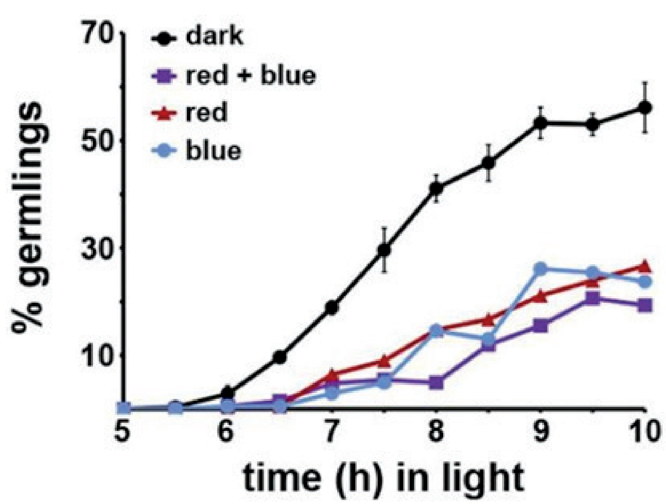

Figure 1. Germination rates of Af293 conidia under constant illumination conditions.[23]

Penicillium and *Eurotium*. Filamentous fungi and actinomycetes are the main microorganisms that cause the biodeterioration of ancient leather artifacts.[2] Compared to bacteria, even under lower temperature and humidity conditions, fungi have a stronger growth vitality and destructive potential. Mold might exist in the form of spores under conditions unfavorable for reproduction and start their life cycle at the proper conditions. In common sense, the contamination of leather by fungi appeared during the long time of storage or burial. However, the contamination during leather processing stages were consistent with the fungi found on ancient leather artifacts, as shown in Table II,[4,26] which proved that a considerable proportion of contamination was from leather processing stages instead of storage.[4] There is a plethora of microorganisms in animal hides from air, water, soil, and feces. These microorganisms exert minimal effects on the hide while the animal is alive, and they will proliferate rapidly after the animal is dead. The proteolytic bacteria in hides could adversely impact the soaking process and leather quality.[27,28] Despite the use of modern tanning methods, microbial contamination is still inevitable. Not to mention collagen-based artifacts that have been in different natural environments for many years, and even centuries.

Biodeterioration mechanisms of leather by fungi

The most common forms of spoilage in leather include the formation of discolored, non-bleachable spots, molds, and holes due to the degradation of leather components such as collagen and water-soluble substances, resulting in a loss of durability and rendering the leather. The collagen and water-soluble substances in the leather might act as essential nutrients for fungi during the proliferation and multiplication of microorganisms at proper relative humidity and favorable temperature.[10,29]

Various fungi, including *Cladosporium*, *Fusarium*, *Aspergillus*, *Penicillium*, and *Mucor*, have been known to attack leather and ancient parchment.[30] Fungi might cause various types of biodeterioration for ancient leather artifacts, which in turn leads to physical and chemical changes. Most reports about fungal deterioration of leather are focused on enzymatic degradation. The proteases, metalloproteinases, and other enzymes they produced could change the softness, properties and structure of leather.[31-33] Fungi such as *Aspergillus niger* and *Penicillium spp.* could produce cellulolytic enzymes to break down the collagen fibers, resulting in the loss of strength, mechanical stability, and flexibility of the ancient leather artifacts. This process could also

Table II

Fungi found on ancient leather artifacts associated with leather process.

Processing	**Damage**	**Source of damage**	**Enzyme optima**[26]	
Biodeterioration before tanning[4]				
Raw hides:	Discoloration	*Halophilic* and other bacteria	pH	Temperature
Green hides		*Micrococcus*		
Salted hides	Putrefaction	*Bacillus*		
Soaking:	Hairslips	*Pseudomonas*		
Liming	Perforation	*Proteus*		
De-liming		*Escherichia*		
Bating				
Biodeterioration after tanning[4]				
Chrome tanning	Colored stains	Moulds	4-4.5	30°C
Wet blue	Mouldy smell	*Aspergillus*		
Vegetable tanning	Lower quality	*Penicillium*		
Fat liquoring	Downgrade of economic value of finished leather	*Paeccilomyces*		
Drying		*Scopulariopsis*		
Finished leather		*Trichoderma*		
		Rhizopus and others		

cause discoloration, brittleness, and changes in the texture of the materials.[34] The fungi such genera as *Arthroderma*, *Aphanoascus*, *Onygena*, *Epidermophyton*, *Microsporum*, *Trichophyton*, *Chrysosporium*, etc., are highly specialized organisms biologically capable of metabolizing horny products of the epidermis with keratin.[35] Under the condition of low water activity, fungi are still able to degrade leather due to their high enzymatic activity and growth ability. In addition, by the accumulation, fungal metabolites would cause pH changes, further promoting the colonization.[29] Additionally, the emergence of various colored spots on materials is usually attributed to a phenomenon, known as foxing. This process involved the discharge and elimination of pigments and acids by fungi, which gave rise to the formation of brown-yellow specks on the surface.[9] The acidic nature of microbial metabolites could instigate the breakdown of collagen fibers and the depolymerization of collagen molecules, resulting in the chemical deterioration of leather, known as acid-deterioration or red-rot. This phenomenon was initially described by Michael Faraday in 1842.[29] Ancient leather artifacts suffered by red-rot typically exhibits a powdery surface, usually tinged with reddish or brownish hues, and a cracked grain structure with partial or total destruction of the grain. The acid metabolites of fungi could further damage the materials to form microcracks and holes.[36] Sometimes, fungal growth might even cause the complete destruction of the artifacts. Moreover, certain microorganisms, such as *Bacillus spp.*, could generate pigments to change the color and reduce the visual appeal.[37,38] Overall, the mechanism of microbial deterioration of leather is complex with various microorganisms and environmental factors. To avoid this deterioration, it is important to design and control the environmental conditions, with the consideration of specific types of microorganisms likely to colonize the leather.

The leather shoe dating back to the 11th-13th centuries was scrutinized by scholars hailing from Art University of Isfahan, Iran.[39] By SEM micrograph analysis, they discovered that hyphae had infiltrated the red stained segment of the leather, prompting the hydrolysis and subsequent flaking of the collagen fibers, thereby leading to the formation of cracks on the surface. The resemblance between this crimson stain and ret-rot was noteworthy, as ancient leather artifacts that underwent combination tanning of vegetable and alum exhibited analogous deterioration features.[39] According to Fontoura *et al.* discoloration caused by fungi might manifest in diverse hues contingent upon the fungal genus and the kind of leather studied such as pickled hide, wet-blue, and vegetable-tanned leather, as shown in Figure 2.[27] Elimination of such stains still pose significant challenges. The SEM microscopy unveiled a marked alteration in the layer structure of the leather. While the uncontaminated samples displayed a smooth and undamaged surface, with distinct pores and fibers, the infected samples exhibited damaged surfaces and irreparable harm. The appearance of variously colored spots stemmed from the discharge of water-soluble pigments by fungi, hydrolysis of fats and oils, and degradation of proteinaceous and hide substances.[27] Alicja *et al.* studied the microscopic morphological deterioration of leather. The leather samples were subjected to high humidity conditions, and after 19 months, their whole structure displayed severe decay. SEM analysis revealed that various microorganisms had solubilized the tanning aggregates encasing the collagen fibers. In addition, evident craters were observed near fungal spores, indicating that the spores could excrete substances capable of dissolving the tanning agent.[29]

Fungi might decolorize leather by attacking the dyes in leather too. The enzyme responsible for this decolorization is laccase.[40] There are various white rot fungi (WRF) that could excrete laccase, including *Dichomitus squalens*, *Ischnoderma resinosum*, *Pleurotus calyptratus*, *Pycnoporus sanguineus*, and *Trametes hirsute*. A new strain called *Trametes villosa* SCS-10 was found to be a significantly active strain in the biodecolorization of leather dyes. Among the strains frequently found on leather artifacts, *Penicillium oxalicum* SAR-3A was reported to degrade a broad spectrum of industrially relevant azo dyes,[41] while *Aspergillus flavus* was capable of decolorizing Azo (Acid red) and Anthraquinonic (Basic blue) dyes.[42]

Conservation and Restoration

Proper preservation and restoration techniques are essential for preventing and controlling fungal deterioration of ancient leather artifacts. Several strategies can be employed to achieve this goal. One of the most effective strategies is to design and control the environment, which involves maintaining optimal temperature and relative humidity levels in museums and archives. It can be achieved by using climate control systems, such as air conditioning and dehumidification systems.[6] Regular monitoring of temperature and relative humidity is crucial for identifying the changes of fungal growth. The standard relative humidity range of 50-65% recommended for artifact preservation in many American and European collections might encourage the further deterioration of degraded collagen in ancient leather artifacts. Therefore, it is recommended to store the ancient leather artifacts at a lower relative humidity of 30% with a cyclic variation of ±5%.[43] Another strategy for preventing fungal deterioration is the use of appropriate storage materials, such as archival-quality boxes and acid-free paper, which could help to prevent fungal growth and to minimize the damage to the artifacts.[44] When it comes to the restoration of ancient leather artifacts that have suffered fungal attack, proper restoration techniques are crucial. These techniques should be able to stabilize and reinforce the leather, preventing further damage and helping to

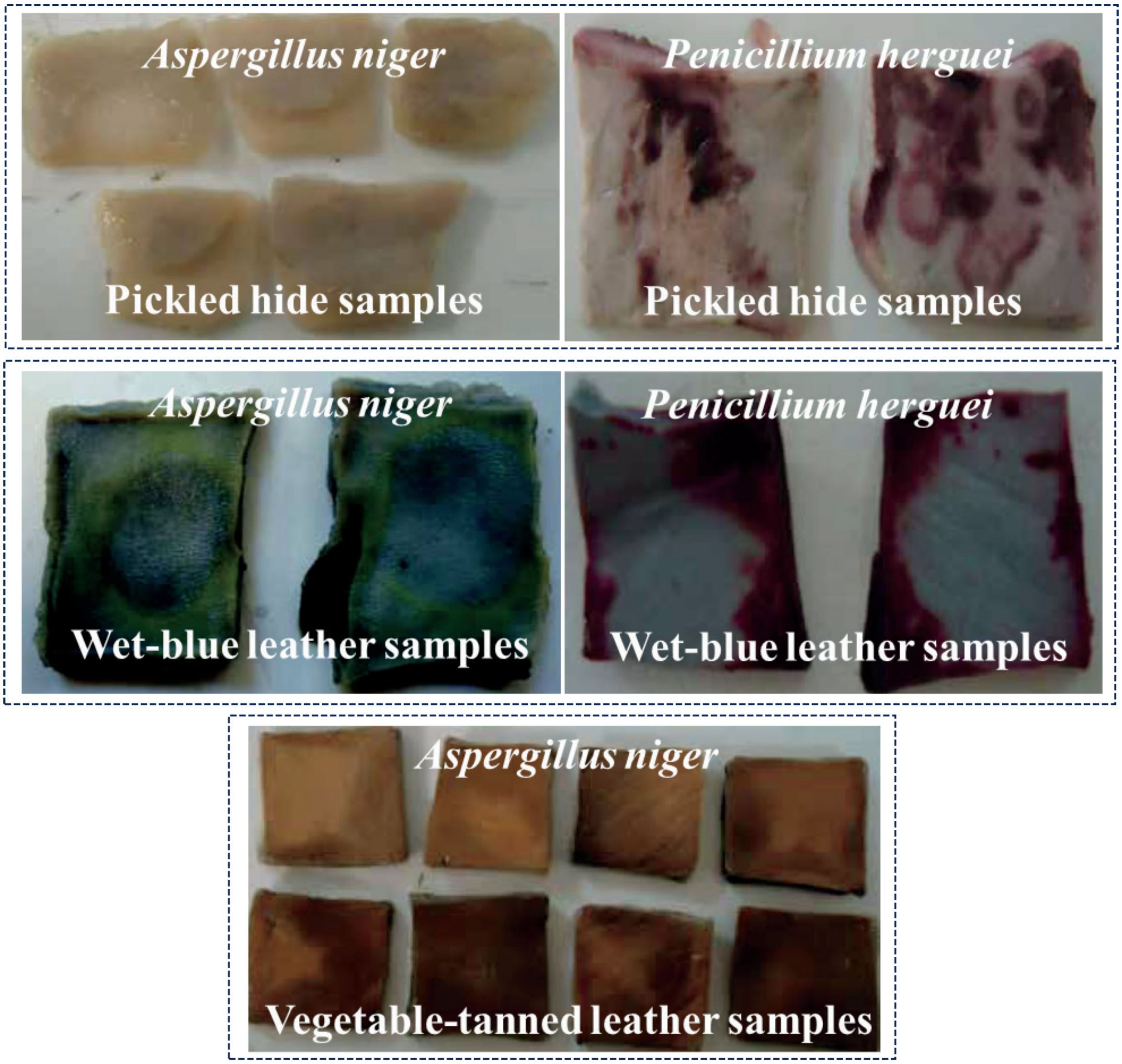

Figure 2. Stains and degradation of pickled hide samples, wet-blue leather samples, and vegetable-tanned leather samples degraded by *Aspergillus niger* and *Penicillium herguei*.

preserve the artifact's original appearance. Conventional methods such as solvent dehydration,[45] freeze-drying,[46] fat liquoring coating[47] and silicone filling[48] have been used, but they might have drawbacks over time, such as becoming hard, brittle, or sticky.[49] Biocides could be effective in preventing and controlling fungal growth, but special caution must be exercised in their use. Some fungicides and disinfectants might be harmful to the artifacts and further damage might be caused. Excessive use of fungicide might also lead to drug resistance.[50] As an alternative, irradiation has emerged as an important technique in the conservation of ancient leather artifacts. Gamma radiation might damage the DNA molecules in microbes, effectively preventing their growth, with little harm to the structure of leather fibers.[51,52] So, it is considered a safer and greener approach, compared to the one using biocides. By these strategies and techniques, it is possible to prevent and control fungal deterioration of ancient leather artifacts.

For the restoration of ancient leather artifacts, special materials with excellent properties might be used to stabilize their structure and increase their properties. Hydroxyapatite (HAp), commonly used as a bone substitute, is biocompatible and can form a cross-linked network structure with collagen, preventing deformation and improving the hydrothermal stability.[53] Nano-hydroxyapatite (nHAp) had good dispersibility because of the nanoparticles, which has been used to repair damaged artifacts, with the flexibility, compactness, and hydrothermal stability of collagen fibers increased.[54,55] Halloysite, a natural nanoclay, is a promising polymer filler because of its good biocompatibility, dispersibility, porosity, as well as high surface area. After dispersing in the polymer matrix, halloysite nanotubes (HNTs) could enhance the tensile strength. The potential of HNTs was demonstrated in the similar thermal stability and fiber cohesiveness in ancient binding leather and artificially aged leather, as well as in repairing fiber pores in ancient paper.[56-58] The current trend in restoring cultural relics involves the use of materials more compatible with similar composition, structure, and properties of leathers.[59] Zhang *et al*. utilized a reinforcement material for decayed leather, significantly improving its physical properties.[60] Nano-collagen produced by the use of chronoamperometry was reported promising in treating vegetable-tanned lambskin leather, with increased mechanical properties, elasticity, softness, and unchanged color.[61] The choice of treatment methods depends on factors such as the type of ancient leather artifacts, the extent of damage, and the desired outcome. However, special attention should be paid to the choice of repairing materials for cultural relic restoration. Further research is needed to explore new materials and techniques for long-term restoration of ancient leather artifacts.

Conclusion and outlook

Fungal deterioration of ancient leather artifacts poses a significant threat to valuable cultural heritage, especially those in museums and archives. Increasing attention has been paid in the restoration and preservation of ancient leather artifacts, and fungal deterioration has been studied with a growing understanding of the deterioration factors. The future research should be focused on the biodeterioration mechanisms and preservation strategies. With the advances in biotechnology and materials science, new and improved preservation methods should be provided for long-term artifact protection with reduced risk of fungal deterioration. However, challenges do still exist, and more effective methods are needed to monitor and control environmental conditions. Deeper and more specific understanding of the fungal growth mechanisms should be studied. Despite these challenges, the study on the fungal deterioration shows a positive outlook due to the recognition of cultural heritage's importance and commitment to preservation. Further research is needed to better know the fungal growth mechanisms and affecting factors for the development of more effective preservation strategies for ancient leather artifacts.

Acknowledgements

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