Fungal degradation of cultural heritages and options for management

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Abstract

Fungi are widely recognized as major biodeteriogens of both modern and historical buildings. Different fungal taxa have been isolated from cultural heritages depending on climatic conditions, humidity level and surface material for fungal colonization. Assimilatory biochemical and non-assimilatory are two mechanisms of heritage material deterioration by fungi. This paper attempts to review information of fungi infesting on historic places across the globe and their management by various biocidal compounds. The preventive methods and potency of various essential oils against fungal growth on cultural materials are also critically reviewed. The available information supports the use of essential oils for the surface treatment or vapour exposure to prevent mould infestation on heritage monuments. Essential oils may also function as fungicidal agents in biocidal formulations/ coatings.

Keywords: Fungi, bio degradation, cultural heritage, biocidal essential oils.

Introduction

Fungi are major agents which cause deterioration of heritage buildings and monuments. Humid conditions encourage fungal biofilm to grow on the surface of the historical buildings and allow to slowly degrading the surface because of its interaction with the products of microbial metabolism[1]. Importance of fungi was highlighted in 1930 from the discovery of antibiotic penicillin by Alexander Fleming[2]. Besides various benefits, fungi also have their disadvantages[3]. It has pathogenicity and responsible for food spoilage, toxin production, infection on humans and bio deterioration of water-damaged buildings[1, 4, 5-6]. Among all the negative effects, our specific concern is a bio deterioration of historical buildings by moulds. Now a day's fungal contamination in houses and building is a complicated problem and shows variable sign like faint of colour, building destruction, unpleasant odour etc. This kind of destruction not only effect houses but also threatens historical monuments and art museums. According to types of deterioration on buildings, the fungi can be classified into four categories [7]. First is plaster fungi which are mostly found in damp bricks and plaster of buildings e.g. *Coprinus spp., Peziza spp.* and *Pyronema domesticum*. Second is stone fungi, mostly found on stone buildings e.g. *Botrytis spp*., *Mucor spp*., *Penicillium spp*. and *Trichoderma spp*. The third type is paint fungi, which cause discolouration of paints in buildings. e.g. *Alternaria alternata*, *Aspergillus spp*., *Aureobasidium pullutans*, *Penicillium spp*., *Cladosporium herbarum*, *Fusarium oxysporum, Phoma violacea* and fourth category is metal and sealants fungi cause disfigurement of metal, glass and sealants. e.g. *Cladosporium resinae*, *Aspergillus niger*, *Aurebasidium pullulans*, *Chaetomium globosum, Geotrichum spp*., *Penicillium luteum*, *Trichoderma viride*[7].

Fungal species involved in deterioration depend on environmental conditions of the area. Temperature, humidity and chemical nature of substratum and low availability of water (a_w) are the main parameters that influence fungal growth[8]. Fungi perform elicit bio deterioration through the penetration of their mycelium into the surface of building material and by the action of metabolic products like organic acids, mycotoxins and pigments, which cause structural change on the building[9, 10]. The rise in population of arthropods in heritage site would subsequently increase the fungal infection level as they contribute to the mortality of arthropods, disposal of organic matter and growth on them[11].

Fungal growth denatures the actual beauty of the heritage monuments. Thus the prevention of fungal growth in a heritage building, as well as the treatment should be taken to preserve them. Limited methods are reported for the control of moulds in buildings. This paper reviews the fungi occurred on the heritage monuments and option for their management.

Fungi on culture heritage

Fungi are present everywhere: air, water and soil and they affect our daily life directly as well as indirectly. Bio-deterioration of cultural heritage is one of them. There are many heritage structures where fungal deterioration were reported not only from India but all over the world. Ancient artwork and paints of building were made of types of organic materials such as egg yolk, casein, linseed, poppy seed etc. These organic substances attract microorganism including fungi and perform as a substrate for their growth. Fungi are the most vicious on building stone, mortar and plaster because of their degradation activity and they are extremely erosive[12]. The list of selected monuments and occurrence of destructive fungi on them are summarized in Table 1.

Table 1.Cultural heritage and their associated fungal flora.

Location	Fungal species	Reference
Ancient museum, Austria	*Aspergillus sp.*	13
Acropolis of Athens, Greece	*Alterneria, Phoma*	14
Marble mouments of the crimea in eastern Europe	*Alterneria, Phoma*	14
Antique temples of delos of Greece	*Alterneria, Phoma*	14
Historical Archive of the Museum of La plata, Argentina	*Scopulariopsis sp. and Fusarium sp.*	15
The Tomas Roig Museum	*Aspergillus, Penicillium and Cladosporium*	16
The Felipe Poey Museum	*Aspergillus, Penicillium and Cladosporium*	16
Gwalior fort, India	*Alterneria, Aspergillus, Curvularia, Penicillum, Fusarium*	17
Sitadevi temple, Deorbija, Chhattisgarh, India	*Aspergillus flavus, A. fumigates, A. niger, A. scalrotium, A. temari, Cladosporiumoxysporum , Curvularialunata, Curvularia clavata, Fusarium sp., Mucor sp., Mycelia sterilia (white), Paecilomycesvariotii, Penicillium chrysogenum, Penicillium sp. , Trichodermaviride*	18
Sandstone monument, Eifell Lock, Serbia	*Bipolarisspicifera*	19
Granite monument, monument of the unknown hero, Serbia	*Epicoccumnigrum*	19
Mahadev temple, Bastar, India	*Aspergillus scalrotium, A. niger, Aspergillusfumigatus, Arcemonium scatrotium, Paecilomycesvarioti*	20
Lascaux cave, France	*Alternaria alternata, Aspergillusfumigatus, A.niger,*	21
Stone monument of Dharmarajika, Taxila	*Cladosporium herbarum, Curvularialunata, Dematium spp., Fusarium oxysporum, Mucorhiemalis, Penicillum, chrysogenum, P. frequentans and Rhizopusoryzae*	22
Mohamed Ali palace, cario, Egypt	*Aspergillusniger, A. flavus, A. fumigates, Penicilliumstolenferme, Fusariumoxysporium*	23
El-Ghory Mosque and Mosque of EL-KadyAbdelbaset, Egypt	*Fusariumoxysporium, Rhizopusoryzae, Cladosporiumherbarum, Alternaria, Stachybotryschartarum*	23
The painted Cave of Lascaux, France	*Fusariumsolani*	24
Cathedral of Salamanca , Spain	*Penicillium, Fusarium, Cladosporium, Phoma and Tricoderma*	25
Chapel of castle herberstein, Styria, Austria	*Acremonium, Engyodontium, Cladosporium, Blastobotrys, Verticilllium ,Mortierella, Aspergillus and Penicillium*	26
Carrascosa del campo church, cuena , Spain	*Penicillium and Fusarium*	27
Parish church of st.Georgen, Styria, Austria	*Acremonium, Engyodontium, Cladosporium, Blastobotrys, Verticilllium, Mortierella, Aspergillus and Penicillium*	26
Caestius Pyramid, Rome, Italy	*Cladosporiumcladosporioides and Alternariaalternata*	28
Pisa tower , Italy	*Sporotrichum*	29
Klippe statues in Hangzhou, China	*Cladosporium, Penicillium, Coniosporium, Alternaria*	30
Arbroath Abbey, Scottish monument	*Cladosporium, Penicillium, Phialophoralignicola*	31
Linlithgow Palace , Scottland	*Acremonium sp. , Penicillium sp.*	31
St. Andrews Castle , Scottland	*Acremonium*	31

Fungal deterioration mechanism on cultural heritage

The colonisation of fungi on the cultural heritage surfaces causes aesthetic and physical damage to sculpture. The deformation of heritage building surface is caused by the presence of a thin layer of dormant/active fungi and their metabolic products such as various acids and pigments. The destruction of monument is altered by type of fungi, nature of surface and surrounding environmental conditions[32]. That's why in tropical areas, or high humid areas, biofilm formation was very frequent[33.] Fungal deterioration caused by three types: chemical, physical and mechanical[34, 35]. Fungal deterioration mechanism consists of diagenesis, colour alteration; oxalate formation; physical penetration of fungal hyphae and destabilization of stone texture, bio weathering by secreted acids; the chelating property of secreted acids[36-44]. The major microbial activities which are responsible for deterioration of constructional material are described in Table 2.

Table 2. Microbial activities involved in deterioration of constructional materials [45].

Microbial activity	Damage Caused	Material affected
Surface growth	Discoloration, water retention	Concrete, ceramic tiles, stone, bricks, plaster, wood, plastic, paints, roofing tiles
Acid production	Corrosion, erosion	Concrete, stone, metal
Hydrolytic enzyme	Increased fragility, erosion	Wood, paint
Chelation	Corrosion, etching	Metal, concrete, stone, glass
Growth of microbial filaments	Physical damage to surface, increase in permeability	Concrete, stone, plaster, painted surface

Discolouration of cultural heritage is primarily due to fungi as they are highly pigmented and their growth may be seen by naked eyes. In physical method, the formations of lesions generally appear on surface. Lesions size up to 2 cm in diameter on the depth of stone was called bio pitting which caused by black fungi[21, 46]. Stones surface inhabited by these fungi appear spotty or even completely covered by black layers due to strong melanisation of the cell walls of these fungi.

Several filamentous fungi like *Aspergillus glaucus* was reported to produce acids on concrete under chemical deterioration method[47]. The SEM investigation revealed that *Fusarium* was responsible for weight loss and calcium release from concrete by the penetration of hyphae into the structure[48]. Stone surface could demineralise by variety of inorganic and organic acid produced by the fungi[49]. Mechanically, filamentous fungi may penetrate the weakened part of a building and more easily when the surface has extra nutrients in the form of dirt or bacterial bio film[50-51]. Granite, calcareous limestone and marble were easily be penetrated by black fungi[21, 46].

In all physical, chemical and mechanical type, building material can be deteriorated by various fungi either directly (using these compound as a nutrient) or indirectly (causing solubilisation through the action of metabolites) [52]. So, bio deterioration on concrete, cement and stone surface are triggered by two mechanisms shown in figure 1. First is direct method called assimilatory biochemical deterioration; occur when fungi use building materials as a source of nutrients and grow on them. The second method is indirect method namely non-assimilatory occur when the metabolites produced by fungi react with the building materials[53]. The indirect method causes solubilisation of building material by the acid production, alkalinity reduction or enzymatic processes[50, 55-57].

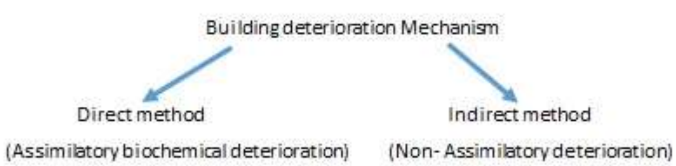

Figure 1. Types of bio deterioration mechanism

There are few external and internal factors are responsible for deterioration of building surface. External factors include climatic conditions such as humidity, temperature, frost and thawing[58].

These conditions alter the growth of microorganism[54, 59-60] whereas kind of microflora present in the environment also affects the degradation mechanism[53]. Internal factor includes type of building material present like concrete, cement, mortar has mineralogical similarities such as calcium silicate, aluminates, silica, aluminium compound, sulphate, mica and feldspars[52]. So, the mechanisms of bio deterioration for all types of materials are same[61].

Conservation techniques

A building can achieve biodegradation resistance by effective and long lasting treatment techniques, which able to inhibit and restrict the growth of bio spore. To preserve architectural conditions, the selection of microbial resistant building materials and protective coating should be preferably guaranteed before applying for the treatment[62]. The important control techniques explained below:

1. ***Surrounding conditions and constructional techniques:*** Bio deterioration process depends upon the material specific like porosity, permeability used in building construction and its environmental conditions. Complete analysis of materials and its processing as well as a detailed study of the surrounding environment like humidity, temperature should be done before constructing the buildings. The protection of building materials against biodegradation may be primarily achieve by the reduction of moisture at infected place and high pressure water or fine-part dry cleaning and application of disinfecting sanitizers (e.g. hydrogen peroxide, eventually combined with conserving agents, iso-thiazole derivatives). Pre-planning is mandatory for control of ron-off water, drainage, roof protection[62]. Water blocking sites should be restricted first before applying any further treatment on the historic buildings**.** The number of arthropod in heritage site directly influence the fungal infection so it would be necessary to reduce their population to decrease fungal contamination as

they contribute for mortality of arthropods, disposal of organic matter and growth of fungal deterioration[11]**.** The treatment method may be helpful for curing from biodegradation. Further treatment has also enhance the resistibility of material against microbes.

2. ***Protective coatings:*** The protecting coating may alter the environmental conditions to reduce microbial growth by reducing humidity and altering surrounding pH. Bio deterioration may be prevent by using microbial resistant materials. Fungi mainly occur in the damp place where moisture content is high. High level of moisture on building materials supports fungal growth[63]. The preservation of historical buildings may be perform using protecting coatings, which can repel water and control moisture level. Application of defensive materials such as plasters, consolidates, water repellants, fillers as well as fixatives and organic binders may be use as per damage situation for preservation[64]. If the threat of microbial infection and subsequent biodegradation processes are proven, the selection of protective solution should consider their microbial resistance to avoid the initiation, reoccurrence or even acceleration of microbial impacts on the materials[65]. Main characteristics of microbial resistant building material are mineral compounds, moisture absorbency, diffusivity and alkalinity. The protective materials used in conservation field have the performance parameters such as transparency, absence of colour, good chemical stability, deep penetration, solidification strength and antiflaking properties. These protective coatings may be acrylic, silane, silicon-based products and hybrid organic materials. The inorganic materials such as silicates of sodium, potassium, lithium and other different compounds have also successfully applied for protection[66-72]. So, the microbial resistance of protecting materials must be preferably tested with material-

specific microbial consortia under laboratory conditions as well as in situ at the materials/objects[73].

3. ***Application of biocides***: To enhance the durability of restoration and conservation treatments on building by bio deterioration processes, the use of biocides as additives might be unavoidable[74]. Antimicrobial active substances can be mainly distinguished between alcohols, aldehydes, organic acids, carbon acid esters, phenols and their derivatives, halogenated compounds, metals and metal-organic substances, oxidative compounds, enzymes, surface-active compounds and various synthetic organic products. The uses of biocides were frequently utilised[75]. Sodium-penta-chlorophenate was found to be effective in controlling the growth of fungi at 2% concentration. It showed 100% inhibition of fungal colonies[76-77]. The list of all effective biocides is presented in Table 3.

Table 3. Name of biocides effective on specific fungi

Biocides	Fungi	Reference
IPA, Biowash, PUFAS, Ima anti, Biosheen, Boramon	*Alternaria alternata, Aspergillus fumigates, A. niger, A. ustus, A. versicolor, Clasosporiumcladosporiodes, C. sphaerosphermum, Penicillumaurantiogriseum, P. chrysogenum, P. simplicissimum, Rhizopusstolonifer, Scopulariopsis candida, Ulocladium, Alternaria*	79
Benzalkonium chloride	*Bipolarisspicifer, Epicoccumnigrum*	18
Dichloro-xylenol (600ppm)	*Aspergillus parasiticus, Fusarium oxysporium, Stachybotrys chartarum*	78
Thymol(700ppm)	*Fusarium oxysporium, Aspergillusflavus, Stachybotrys chartarum*	78
Penta- chlorophenol (400ppm)	*Aspergillus fumigates, Aspergillus oryzae, Penicillium oxalicum, Acremonium kiliense*	78
Sodium Azide(100ppm)	*Fusarium oxysporium, Aspergillus parasiticus, A. niger*	78
p-cresol (600ppm)	*Aspergillus niger, A. oryzae, Fusarium oxysporium*	78
Hetrerocycle pyrazolo pyrimidine derivatives	*Aspergillus. niger, A. flavus, Penicillium frequentans and P. granulatum*	80

4. Antifungal essential oils from plants

Biocides are toxic chemicals which can affect both microbes and higher organism including humans. Most common fungi *A. alternata* shows inhibition by essential oils of *Abies sibirica, Thymus pulegiodes, Carum carvi, Mentha piperita, Citrus bergamia, Eucalyptus globulus, Syzygium aromaticum*[69]. Clove oil found to be effective against most building fungi whereas vapours of peppermint oil were reported against *Sclerotinia*[81-82]. Clove oil also has antifungal activity at a concentration up to 25 %[83-85]. The antimicrobial activity of clove is attributed due to presence of eugenol (2-methoxy-4-allyl phenol). This compound has a wide spectrum of antimicrobial effect[86].

The volatile essential oils of *Citrus aurantifolia* and *C. reticulata* have significant antifungal potency against building fungi[87]. The anise and garlic oils showed the best anti-fungal effect against fungi on Cuban and Argentine heritage whereas oregano oil was even able to inhibit sporulation of fungi[83]. The list of essential oils exhibited anti-fungal potency against a range of fungi are shown in Table 4. These studies reveal that many essential oils possess antifungal activity against monument associated fungi. These finding support the application of essential oils for surface treatment[95].

Table 4. Name of Essential oil work against specific fungi.

Essential oil Name	Effected on fungi	Reference
Abies sibirica	*Alternaria alternata, Aspergillus niger, Aspergillus versicolor, Cladosporium sphaerospermum, Penicillium chrysogenum, Penicillium simplicissium, Rhizopus stolonifer*	79
Thymus pulegiodies	*Alternaria alternata, Aspergillus niger, Penicillium chrysogenum, Penicillium simplicissium, Scopulariopsis sp., Fusarium sp.*	79, 15
Carumcarvi	*Alternaria alternata, Aspergillus niger, Aspergillus versicolor, Cladosporiums phaerospermum, Penicillium chrysogenum, Penicillium simplicissium*	80
Mentha piperita	*Alternaria alternate, Aspergillus versicolor, Cladosporium sphaerospermum, Penicillium chrysogenum, Rhizopus stolonifer, Mucor racemose, G. candidum, A. niger*	79,88,89
Citrus bergamia	*Alternaria alternata, Aspergillus versicolor, Penicillium chrysogenum, Penicillium simplicissium*	79
Eucalyotus globules	*Alternaria alternate, Aspergillus versicolor, Cladosporiumsphaerospermum*	79,88
Syzygium aromaticum	*Alternaria alternata, Aspergillus niger, Aspergillus versicolor, Cladosporium sphaerospermum, Penicillium chrysogenum, Penicillium simplicissium, Rhizopus stolonifer*	79,89
Carumcopticum	*Penicillium sp., Fusarium sp., Curvularia sp., Alternaria sp., Aspergillusnidulans*	17
Ocimum sanctum	*Penicillium sp., Fusarium sp., Curvularia sp., Alternaria sp., Aspergillusnidulans*	17
Cinnamomum zeylanicum	*Penicillium sp., Fusarium sp., Curvularia sp., Alternaria sp., Aspergillusnidulans*	17
Pinuspinaster	*Penicillium sp., Fusarium sp., Curvularia sp., Alternaria sp., Aspergillusnidulans*	17
Cedrusdeodara	*Penicilliumsp , Fusariumsp ,Curvulariasp , Alternaria sp., Aspergillusnidulans*	17
Syzygium aromaticum	*Aspergillus niger, Aspergillus clavatus, Penicillum sp., Fusarium sp.*	89
Origanumvulgare	*A. niger, A. clavatus, Penicillum sp., Fusarium sp.*	89
Allium sativum	*A. niger, A. clavatus, Penicillum sp., Fusarium sp.*	89
Pimpinellaanisum	*A. niger, A. clavatus, Penicillum sp., Fusarium sp.*	89
Origanumvulgare	*Scopulariopsis sp., Fusarium Sp.*	15
Rosmarinusofficinalis	*Bipolaris sp., Epicoccumnigrum*	19
Lavandulaangustifolia	*Bipolaris sp., Epicoccumnigrum, Penicillium sp.*	19
Citrus limon	*Aspergillus niger, Geotricum candidum*	89
Artemisia nilagirica	*Aspergillus flavus, A. niger, Fusarium, Penicillium notatum*	90
Ageratum conyzoides	*Didymellabryoniae, Rhizoctonia solani*	7,91
Ailanthus excelsa	*Candida albicans, Saccharomyces cevervidiae*	7,92
Albizialebbeck	*Candida albicans and Saccharomyces cerevisiae*	7,92
Artemisia annua	*Candida albicans*	7,92
Caesalpiniacristata	*Candida albicans*	7,92
Calotropis gigantean	*Rhizoctonia solani, Candida albicans*	7,92,93
Medicagosativa	*Cladosporium cladosporoides*	80,94

5. Alternative techniques

Microwave heating system can also showed effective results at 2.45 GHz microwave electromagnetic radiation against fungal contamination. This method was very effective at 65ºC for 3 minutes[93]. The nano-silver suspension at 5-15ppm exhibited effective result as biocide. Thus nano-silver additive in paints and coatings make it possible to prevent the growth of fungus[94]. The water repellent coating with antifungal essential oil may be another solution to prevent fungal deterioration. Concrete sealers like liquid sealer LS-S, Magik impregnator, WEB-CBX, RIK- Seal medium Gloss, KONEX WRA- 2318, Evercrete DPS, La Guard PWC with essential oil of peppermint and eucalyptus were tested as antifungal coatings against wall fungi[87]. The antifungal properties were showed by super-hydrophobic nanoparticles with or without essential oils like arborvitae, oregano and thyme oils to reduce the growth of moulds[96]. The latest alternative is green nanotechnology in which *Bacillus* species produces metabolites with antifungal activity. It may be sustainable option because it is eco-friendly and harmless to human [95-97].

Conclusion

Historic monuments are our heritage. Microbial contamination not only slowly deteriorates monuments but also vanish our culture hidden on them. The correct identification of fungal organism is important as not all fungi are equally destructive. The profuse number of fungi involved in the deterioration process based on climate condition and material of heritage monuments but the predominant fungi are *Aspergillus, Fusarium, Cladosporium, Curvularia* and *Penicillium*. There are three types of fungal deterioration process: Physical, chemical and mechanical. The deterioration processes two separate principles of mechanism. First is direct method known as assimilatory biochemical deterioration in which fungi can use monument material as a source of nutrients and grow on them whereas second is the indirect method also known as the non-assimilatory method, occurred when the metabolites produced by fungi react with the building materials. Fungi colonize both inorganic and organic surfaces and try to survive and multiply according to the nature, humidity, temperature and availability of water on the surrounding. All these variables influence the number and diversity of species involved in deterioration pattern (discoloration, acid production, corrosion, chelation, etc). The conservation of the heritage monument is a complex process, dealing with an extremely heterogeneous range of elements. Due to excessive variables treatment of fungal deterioration is a challenging task and need immediate action. The cleaning of the heritage site may be useful to prevent fungal deterioration in the initial stage. Protective coatings e.g. water repellant, organic binder and fixatives may be applied to the monuments building but parameters such as transparency, chemical stability, penetration, solidification should remain in mind before use. Sometimes susceptible materials present in the coating, themselves attacked by fungi. To hinder this problem, biocides must be utilize. The fungicide can penetrate the pores of building surface without the hassle and remain for 2 to 5 years depends upon their chemical composition. Inorganic nanoparticles e.g. Ag_2O, TiO_2, ZnO, etc have better possibilities to preserve cultural heritage. Toxicity of chemical biocides not only kills microbe, besides attack on human health and the environment. Despite the fact, eco-friendly treatment may be an excellent alternative to conserve monuments. Green biocides from natural fount propound may be an alternative to the toxic chemicals. The specific organisms like *Bacillus* genus have been suggested as decontaminating approach against fungal deterioration but future interrogation is needed to supervise the harmlessness and effectiveness of this approach. The anti-fungal potential of numerous essential oils also exhibited influential results on fungal contamination. There are a variety of reasons that phytochemical may be considered to control fungal growth on heritage structure. Further studies on essential oils based green biocide would be useful to develop eco-friendly, renewable, cost-effective, long-lasting, and feasible protecting coating which give the better treatment fir fungal problem in heritage buildings.

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