International Biodeterioration & Biodegradation 126 (2018) 86–94

Contents lists available at ScienceDirect

International Biodeterioration & Biodegradation

journal homepage: www.elsevier.com/locate/ibiod

Effect of biological colonization on ceramic roofing tiles by lichens and a combined laser and biocide procedure for its removal

J. Pena-Poza[a], C. Ascaso[b,**], M. Sanz[c], S. Pérez-Ortega[d], M. Oujja[c], J. Wierzchos[b], V. Souza-Egipsy[e], M.V. Cañamares[e], M. Urizal[f], M. Castillejo[c], M. García-Heras[a,*]

[a] Instituto de Historia (CCHS-CSIC), Calle Albasanz 26-28, 28037 Madrid, Spain
[b] Museo Nacional de Ciencias Naturales (MNCN-CSIC), Calle Serrano 115bis, 28006 Madrid, Spain
[c] Instituto de Química Física Rocasolano (IQFR-CSIC), Calle Serrano 119, 28006 Madrid, Spain
[d] Real Jardín Botánico (RJB-CSIC), Plaza Murillo 2, 28014 Madrid, Spain
[e] Instituto de Estructura de la Materia (IEM-CSIC), Calle Serrano 121, 28006 Madrid, Spain
[f] Thor Especialidades SA, Barcelona, Spain

ARTICLE INFO

Keywords:
Biodeterioration
Ceramic roofing tiles
Lichens
Removal procedures
Laser irradiation
Biocide Acticide® CF

ABSTRACT

Biodeterioration damage is an important issue in conservation and restoration of built heritage, especially when ceramic materials are used. Biological colonization of ceramic roofing tiles by lichens is a common phenomenon. However, there are no reports to date of lichens removal from unglazed roofing tiles for conservation purposes. This paper for the first time reveals the results of a combined procedure undertaken to assess the removal of lichens on different kinds of unglazed ceramic roofing tiles by treatments based on both dual sequential laser irradiation and treatment using Acticide® CF biocide. Three species of lichens were identified: *Verrucaria nigrescens*, *Calogaya decipiens* and *Pyrenodesmia teicholyta*. The chemical and mineralogical composition of roofing tiles were characterized by X-ray fluorescence (XRF) spectrometry, optical polarized petrographic microscopy, and X-ray diffraction (XRD). Laser irradiation was accomplished by applying sequences of nanosecond laser pulses at two wavelengths (1064 and 266 nm). After dual sequential laser irradiation a biocide was applied. To assess the combined effect of both treatments several techniques were used, including stereo and fluorescence (FM) microscopies, scanning (SEM) and transmission (TEM) electron microscopies, and FT-Raman spectroscopy. Chemical composition of the analyzed roofing tiles was shown as a relevant factor regarding the degree of interaction between the biological colonization and the substrate, and hence, the bioweathering effect. The combined procedure has proved to be very effective in ablating cortical layers in all species, or even complete areolae in *V. nigrescens*, enhancing biocide effect in the thalli of *C. decipiens* and *P. teicholyta*, and producing the complete damage of both bionts.

1. Introduction

A wide biodiversity has been recognized in architectural ceramic materials such as bricks, roofing tiles and glazed wall tiles. This biodiversity very often causes biodeterioration on these materials which in turn induce not only aesthetic but also chemical and physical damage. Decay by biodeterioration is an important issue in conservation and restoration of built heritage, especially when ceramic materials were used (Warren, 1999).

Different types of biological colonization have been identified in such materials, from microorganisms to plants, including bacteria, cyanobacteria, algae, lichens and fungi (Coutinho et al., 2015). Regarding biodeterioration damage, bricks are the most studied type of architectural ceramic material (Wang et al., 2011), while roofing (Gazulla et al., 2011) and glazed wall tiles (Coutinho et al., 2013) are hardly investigated. In addition, biodeterioration of stained glass windows have been also reported (Carmona et al., 2006). Studies focused on the impact of the lichen thalli on a monumental stone substrate have revealed a high bioreceptivity of rocks to lichen colonization depending on rock surface roughness, porosity, and capillarity, as well as a strong incidence of lichens in the biodeterioration of stone built heritage (de los Ríos et al., 2004; 2009).

Ceramic roofing tiles have been traditionally elaborated from a composition very similar to that used for bricks, that is, an uncoated or

* Corresponding author.
** Corresponding author.
E-mail addresses: ascaso@mncn.csic.es (C. Ascaso), manuel.gheras@cchs.csic.es (M. García-Heras).

http://dx.doi.org/10.1016/j.ibiod.2017.10.003
Received 23 December 2016; Received in revised form 6 October 2017; Accepted 10 October 2017
0964-8305/

unglazed body mainly composed of illitic-kaolinitic clays with quartz and a variable amount of carbonates which is subsequently fired at low/medium temperatures. The main function of roofing tiles is to protect the building against rain and sun and, due to this reason they are commonly exposed to weathering and biological agents which later may cause biodeterioration. Fired clay roofing tiles were first used in Egypt and other ancient civilizations such as Babylon. However, Romans were probably the ancient people which more extensively roofed their buildings. Although the technique of glazed roofing tiles was already known by Babylonians it was widely spread later by the Islamic influence in medieval times (Campbell and Pryce, 2003).

Biological colonization of ceramic roofing tiles by lichens is a frequent and common phenomenon. However, this kind of colonization over the ceramic roofing tiles has been scarcely described (Kiurski et al., 2005). It affects not only the aesthetic aspects of the building roofs but also roof functionality can be affected by lichens cover (Laiz et al., 2006). For this reason any study related to the removal of lichens from roofing tiles may be of significant importance, even for roofing tiles conservation purposes. Removal procedures of biofilms composed by algae, cyanobacteria and fungi with application of four biocides have been evaluated, but in glazed majolica tiles, by Coutinho et al. (2016). However, the process of lichens eradication from ceramic roofing tiles has never been reported up to date.

In this study it is hypothesized that biological weathering (lichen thalli) of ceramic roofing tiles made by traditional methods of elaboration depends on the characteristics of the substrate (uncoated or unglazed ceramic). The usefulness of combined treatments using dual sequential laser irradiation and biocides is further assessed in order to help decision making in conservation and restoration of historical buildings in which ancient or traditional ceramic roofing tiles need to be necessarily preserved.

Laser cleaning is a well-established technique because it provides fine and selective removal of superficial deposits and encrustations such as biological and black crusts on stone substrates (Cooper, 1998; Maravelaki-Kalaitzaki et al., 2003; Tornari et al., 2006). In the case of lichen elimination, laser cleaning constitutes a promising alternative to more conventional cleaning techniques (de Cruz et al., 2009; Speranza et al., 2013; Osticioli et al., 2015). This technique has been also used for the elimination of dark deposits originated from air pollution on terracotta substrates, with close composition to ceramic roofing tiles (Oujja et al., 2005).

2. Materials and methods

2.1. Ceramic roofing tile samples

Three unglazed ceramic roofing tiles coming from Segovia (samples 1 and 2) and Guadalajara (sample 3) provinces located in the center of Spain under a mesothermal climate were selected to undertake this research. All of them belonged to traditional rural built heritage and were elaborated following traditional methods. They have been naturally exposed to both weathering and biological agents for years and all showed an extensive biological colonization on their surfaces (Fig. 1).

Ceramic body samples from roofing tiles were characterized by the following techniques: X-ray fluorescence (XRF) spectrometry, optical polarized petrographic microscopy through thin-section examination, and X-ray diffraction (XRD).

Chemical analyses by XRF were carried out with a PANalytical Axios wavelength dispersed X-ray spectrometer equipped with a rhodium tube of 4 kW and 60 kV. Analytical determinations were undertaken through the standard-less analytical software IQ+ (PANalytical) from synthetic oxides and natural minerals. Thin-sections for petrographic observations were cut perpendicularly to the surface of the roofing tiles. The observations were accomplished with a Kyowa Bio-Pol 2 polarizing light microscope. Micrographs from thin-sections were recorded with a Moticam 2500 camera. XRD analyses were carried out with a PANalytical X'Pert-MPD unit using Kα of copper radiation (1.54056 Å), under set conditions of 45 kV and 40 mA. Diffractograms were obtained between 2θ = 5–60°. Both XRD and XRF analyses were carried out on powder samples prepared by grinding ceramic body roofing tile fragments, with their most external surfaces removed to avoid contaminations by biocolonization, in an agate mortar.

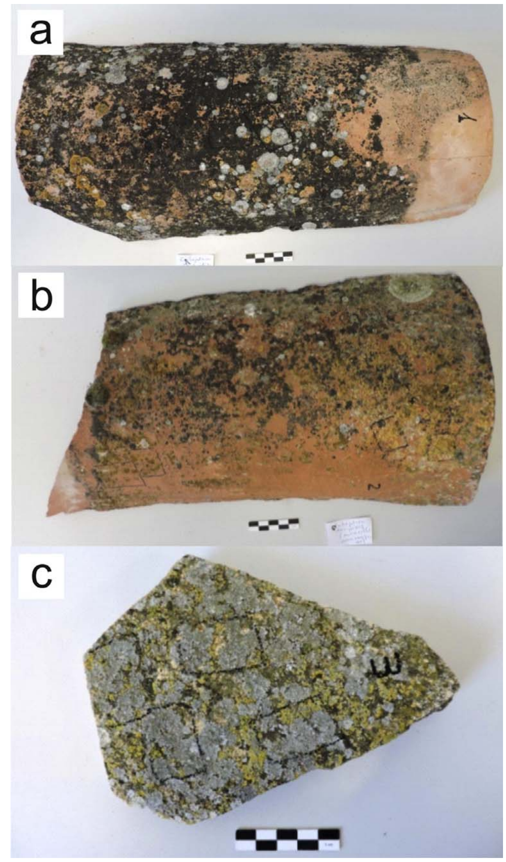

Fig. 1. Ceramic roofing tiles studied. a) Tile sample 1. b) Tile sample 2. c) Tile sample 3.

2.2. Procedures for the removal of the lichen thalli

Lichen thalli were treated according to two different procedures: dual sequential laser irradiation alone and dual sequential laser irradiation plus chemical treatment containing an Acticide® CF biocide. The most effective of the two procedures was the second one. Consequently, the results and discussion of this paper will be focused on this combined procedure. However, as control, untreated and only chemically treated thalli were also tested.

Regarding the best laser treatment to remove lichen thalli, some authors have reported dual IR-UV sequential irradiation at 1064 and 355/266 nm as the ideal treatment to eliminate lichen colonization crusts while ensuring preservation of the lithic substrate (Sanz et al., 2015, 2017). In the present study, dual IR-UV sequential irradiation at 1064 and 266 nm has been applied. The wavelength of 1064 nm was selected because it is known that it produces ultrastructural changes and therefore metabolic damage in the mycobiont hyphae penetrating stone substrates (Speranza et al., 2013), whereas the 266 nm wavelength is adequate because lichen specimens usually present larger light absorbance at this wavelength (Nguyen et al., 2013; Sanz et al., 2017). Dual sequential irradiation was carried out with a Q-switched Nd:YAG laser (pulse width 17 ns, repetition frequency 1 Hz) using the fundamental wavelength of 1064 nm and its fourth harmonic at 266 nm.

Sequences of 50 IR pulses followed by 50 UV pulses under the same irradiation path were applied in each treated area. The unfocussed laser