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Wavelength effects on the laser removal of lichens on heritage stone

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Lasers constitute a promising alternative to more conventional cleaning techniques for certain applications. In fact laser cleaning of stone is a well-established technique in the field of cultural heritage because it allows fine and selective removal of superficial deposits and encrustations. When biodeterioration crusts are present on the stone surface, the laser approach requires a physical parametrization, associated with a diagnosis of the induced effects on the both stone and biodeteriogens [1, 2]. Lichens (symbiotic association of a fungus with a photosynthetic partner, an alga and/or cyanobacteria) develop complex interactions with the rock minerals and, depending on the species, present characteristic morphologies that influence the resistance to the removal treatments.

In this work, granite from Alpedrete (Madrid) quarry front and sandstone from Valonsadero (Soria) were investigated in order to find the conditions for efficient laser removal of lichens crusts. These stone materials have been traditionally used in heritage buildings and monuments in central Spain. The selected samples present superficial areas colonized by different crustose lichens, i.e. Protoparmeliopsis bolcana, P. muralis, Aspicilia viridescens, A. contorta, Candelariella vitelina and Rhizocarpon disporum.

To determine the best laser irradiation conditions, we measured UV-Vis absorption spectra of the lichen crusts diluted in ethanol. A comparative laser cleaning study was carried out on the mentioned samples with nanosecond laser pulses of infrared, ultraviolet and sequences of both wavelengths. To that purpose we used the fundamental (1064 nm), 3rd (355 nm) and 4th (266 nm) harmonics of a Q-switched Nd:YAG laser (pulse duration 17 ns, repetition rate 1-10 Hz) at fluences just below the previously determined ablation thresholds.

A number of techniques were employed to detect morphological and chemical changes on the irradiated surfaces. Stereomicroscopy was used to describe morphological and colour changes. Scanning electron microscopy (SEM) at low vacuum served to analyse the effects on the surface of the lichens, while SEM-BSE of the polished transversal cross sections was applied to assess effects inside the crust and in the lithic substrate. FT-Raman spectroscopy was employed to detect possible structural and chemical changes.

The results obtained indicate that the optimal conditions for laser removal of the lichen crusts are highly dependent of the lichen species treated. For example, in the case of Protoparmeliopsis, sequential 1064-266 nm laser irradiation partially removed the thallus cortex in the vegetative parts of the lichen (areoles). However, the damage inflicted in the apothecia (fungal reproductive structures) was found minimal, possibly due to the highly efficient protective role of their sterile elements. For the other lichens, the optimal cleaning conditions were obtained at 266 nm, which resulted in the partial removal of the cortex and exposition of the algae. In this case the complete removal of fragments of thalli was observed.

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[2] Sanz M. et al., Appl. Surf. Sci. **346** (2015) 248.