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In situ evaluation by colour spectrophotometry of cleaning and protective treatments in granitic Cultural Heritage

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ABSTRACT

This paper is focused on the reliability of the colour spectrophotometry as a non-destructive *in situ* technique to evaluate the cleaning effectiveness. A biofilm composed by filamentous green algae and cyanobacteria developed on a granitic building located in NW Iberian Peninsula was removed using different cleaners commonly used by professionals in stone conservation (distilled water, ethanol, benzalkonium chloride, *Hyvar X*, ethanol, sodium hypochlorite and the commercial products *Limpia-Fachadas1* and *Biocida*). Also, the durability of some water repellents applied after the cleanings was evaluate. The colour measurements expressed in the CIEL*a*b* colour space were performed before and after the cleanings and after the water repelling products application, at eight moments during two years (since June 2011 until June 2013) of exposition under a temperate humid climate.

As general results, the colour spectrophotometry resulted in a reliable method to monitor the cleaning effectiveness, allowing to identify the most effective methods, but also the rate of the recolonization of the granitic surface during time. However, this technique was not recommended as re-growth indicator when water repellents were applied after the cleanings, due to the impact produced by the products on the colour of the stone.

1. Introduction

As in the outcrops, the Cultural Heritage stones can be colonized by living organisms, mainly bacteria, algae, fungi and lichens, inducing the biodeterioration of the stones since the materials show modifications of their properties due to physical and chemical processes (Adamo and Violante, 2000; Warscheid and Braams, 2000; Sabbioni et al., 2003; Bonazza et al., 2005; Crispim and Gaylarde, 2005; Gaylarde et al., 2007).

In NW Iberian Peninsula, the temperate humid climate favours the colonization by organisms of monuments and facades compromising the stone durability (Prieto et al., 2001, 2007; Lisci et al., 2003; Prieto and Silva, 2005).

Cleaning is a fundamental procedure in Stone Conservation and it does not concentrate on the extraction of the superficial crust or patina since it also has to try to eliminate the origin of this alteration or at least, mitigate its effects, involving the application of repair and protection products in order to avoid a new cleaning intervention (Doehne and Price, 2010; Pozo-Antonio et al., 2016; Ruffolo et al., 2017). Chemical products can be applied on the stone to remove or dissolve dirt or to kill/reduce colonizing microorganisms. In order to avoid damages to the stone material, it is necessary to know the properties of the chemical products, their concentration, application procedure and possible effects on the stones (Warscheid and Braams, 2000; Doehne and Price, 2010). Many studies based on cleaning effectiveness, mainly in carbonate stones, have been carried out *in situ* and some authors recommended the use of re-treatments in order to avoid biological proliferation (Nugari and Salvadori, 2003; Tretiach et al., 2007; Cuzman et al., 2008; Sanmartín et al., 2011; de los Ríos et al., 2012).

After the cleaning, the usual protocol to follow in order to protect the stone consists on the application of water-repellent products to avoid as much as possible the entrance of water into the

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porous system of the stone (Tsakalof et al., 2007; D'Arienzo et al., 2008; Vacchiano et al., 2008). Although the entrance of liquid water into the stone is avoided, the exchange of water vapour with the environment has to be permitted, because if water accesses to the stone, it may also leave in form of water vapour. After the cleaning or water repelling treatments different *in situ* techniques are required to be applied in order to evaluate the cleaning effectiveness or follow the recolonization of the surface to study the durability of the treatments performed.

Colour spectrophotometry was successfully applied from 1990s as a non-destructive technique to *in situ* evaluate the growth of microorganisms on stones and then, the effectiveness and durability of protective (water-repellent products application), consolidation and cleaning treatments (Alessandrini et al., 2000; Tretiach et al., 2007; de los Ríos et al., 2012; Pinna et al., 2012). In the case of granite, which is the most common building stone of NW Iberian Peninsula, the studies based on colour spectrophotometry to evaluate different treatments are scarce and not very recent (Rivas et al., 1998, 2009, 2011a; Silva et al., 2000; Prieto et al., 2008). The intrinsic properties (texture, mineral composition and porosity) of this kind of stone also influence on the effectiveness and durability of the consolidant and water repellent treatments (Mosquera et al., 2009; de Rosario et al., 2015).

With regards to the application of colour spectrophotometry for the control and quantification of the biological colonization after cleaning treatments, several studies can be emphasized. The suitability of colour measurement to quantify the biomass of phototrophic organisms was successfully proved by means of in vitro colour measurement of chlorophyll-a and fluorescein diacetate (FDA) hydrolysis (Prieto et al., 2004). There are also several studies that demonstrate the reliability of colour spectrophotometry to detect the early biological colonization on stones, even when it is not detectable under naked eye (Prieto et al., 2002, Prieto and Silva, 2005). Lately, Prieto et al. (2010a, b) developed different methodologies based on the relationship between colour of the granite and cyanobacteria. Moreover, Sanmartín et al. (2011) have proved the suitability of colour spectrophotometry in order to estimate the chlorophyll degradation as a result of biocide treatments and to detect and quantify microorganisms on granitic buildings (Sanmartín et al., 2012).

Definitely, the majority of the studies about the use of colour spectrophotometry was focused on the evaluation of the recolonization of stones after biocides application; nevertheless, this analytical technique is less used to evaluate the recolonization of the stones after water-repellent treatments (Alessandrini et al., 2000; Pinna et al., 2012), being those studies centred on the evaluation of mixtures of water-repellent products with biocides in substrates different to granite, i.e. limestone, marble and sandstone.

Due to the scarce studies focused on granites and on the influence of the texture on the colour characterization, it is of interest to investigate the reliability of the colour spectrophotometry as a non-destructive technique to *in situ* evaluate the cleaning effectiveness and the durability of water repelling products on granitic stones over time. The current article describes the application of this non-destructive technique to *in situ* evaluate the cleaning effectiveness achieved by different cleaners and also the durability of water repelling products applied before those on a wall composed of a granitic stone commonly used in the Cultural Heritage of the NW Iberian Peninsula. The method was based on naked eye observations and the computation of the colorimetric variations of the parameters in CIEL*a*b* colour space during two years in order to determine the best cleaners and water repellents on granitic Cultural Heritage. Also, it was determined the influence of different water repellent products on areas previously cleaned on the stone colour.

2. Materials and methods

2.1. Granitic wall and biological colonization

The present study was carried out on the perimeter wall of Higher School of Conservation and Restoration of Cultural Heritage of Galicia (in Galician: *Escola Superior de Conservación e Restauración de Bens Culturais de Galicia,* hereinafter ESCRBCG) located in Pontevedra (NW Spain). This coastal city (82,500 hab.) has a temperate humid climate, with rainy winters (1600 mm rainfall) (Martínez Cortizas and Pérez Alberti, 1999). The average annual temperature is 14 °C, with cold to moderate winters (10 °C) and moderate summers (20 °C) and an average relative humidity of 70 ± 5% (Martínez Cortizas and Pérez Alberti, 1999). The wall is built of granite (Fig. 1a and b) and the studied side was the SW facing side (Fig. 1a). Therefore, at this latitude, the selected side receives the direct insolation during a greater number of hours during the day (especially in summer time) than during the rest of the year. Moreover, the humid climate contributes that during autumn and winter, the wall remains wet for a long time, favouring the biological colonization.

The granite was extracted from an ancient quarry located near the city; from the geologic point of view, this rock is classified as a medium-grained granite of alkaline affinity (IGME, 1985) composed of quartz, plagioclase, potassium feldspar, muscovite, biotite as principal minerals and sillimanite, andalusite and apatite as accessory minerals. Grain size for the different minerals ranges from 0.4 to 5.0 mm (Fig. 1b) (IGME, 1985). A sample of the stone from the wall was taken and it was determined that the open porosity (accessibility to water following RILEM, 1980) was 4.41% and Hg-accessible porosity (PoreMaster-60 device of Quantachrome Instruments with two pressure units Pascal 140 and Pascal 440) was 5.95%. The difference between both values reflects the existence of certain percentage of pores not accessible to water.

A sample of the colonized stone from the wall was taken in order to characterize the nature of the colonization by means of optical microscopy (OM, SMZ800 Nikon), petrographic microscopy (PM, Nikon Alphaphot-2 YS2) and scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM-EDS, Philips XL30 and JEOL JSM-6700) working in backscattered electron (BSE) and secondary electron (SE) modes. Filamentous green algae and cyanobacteria (Fig. 1 c–e) were the organisms responsible of the colonization. Cross section visualization under PM confirmed that the thickness of the patina reached 10 μm (Fig. 1 c–d) and allowed to describe the algae cells penetration through mineral grains (Fig. 1d). Under SEM, numerous filamentous structures were observed (Fig. 1e).

2.2. Cleaning procedures

For the application of the cleaners selected, eight cleaning areas of 15 × 10 cm^2 were distributed on the wall in areas with the same level of biological coverage (Table 1 and see Fig. 1h): areas B–F (trial cleanings I) and areas E, J and H_2O (trial cleanings II). An additional area (area A, trial cleanings I) was selected for control purposes, i.e. without any product application.

Before the cleaning performance, colour of each area was characterized in CIEL*a*b* colour space (CIE S 014-4 / E, 2007) by means of a Minolta CM-700d spectrophotometer. The coordinate L* represents the lightness in values ranging from 0 (black) to 100 (white) and coordinates a* and b* express the colour wheel, taking values ranging from +a* (red) to - a* (green) and from +b* (yellow) to - b* (blue). Moreover, it was computed the parameter C^*_{ab}, the chroma or colour saturation, which expresses the relative strength of a colour, and its value corresponds to $C^*_{ab} = [(a^*)^2+(b^*)^2]^{1/2}$.