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Comparison of a bio-based corrosion inhibitor versus benzotriazole on corroded copper surfaces

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ABSTRACT

This research aims to characterize and compare the protective behaviour of a bio-based treatment versus benzotriazole (BTA) for the preservation of copper-based artefacts affected by active corrosion induced by copper chlorides. For this, the treatments were applied on artificial copper hydroxychlorides produced on copper sample. Their inhibition performance was then investigated by Scanning Electron Microscopy, Infrared Spectroscopy and Electrochemical Impedance Spectroscopy. Results showed few BTA-Cu complexes formed and poor protectiveness of the BTA treatments. In contrast, the bio-based treatment resulted in the conversion of almost all copper hydroxychlorides into copper oxalates, providing a more efficient corrosion inhibition.

1. Introduction

Artefacts made of copper and its alloys undergo progressive and inevitable corrosion processes. Therefore, the identification of the degradation mechanisms and of the corrosion products involved thus is important to select the more adequate conservation-restoration approach [1]. One of the most harmful degradation phenomena observed on copper substrates is the so called "bronze disease" [2]. This corrosion process is caused by the interaction between copper and chloride ions in presence of oxygen and at high relative humidity producing nantokite (CuCl) [2]. The formation of nantokite in the presence of air and moisture causes a cyclic corrosion process that produces a green powdery layer of copper hydroxychlorides $Cu_2(OH)_3Cl$ on the artworks [3–5]. This corrosion product has three main polymorphic crystal forms: atacamite, clinoatacamite and botallackite [6]. Although copper hydroxychlorides are generally stable, in some cases, chloride ions can be released from $Cu_2(OH)_3Cl$ and lead to further corrosion of the artefact [2]. This cyclic reaction is the main cause of stress cracking, material loss and eventually the complete loss of the object.

In metal conservation, the use of corrosion inhibitors to decrease the corrosion rate of copper-based relics is a common practice [2]. The most largely used product for copper-based objects is benzotriazole (BTA) that has, for a long time, been considered as the reference corrosion inhibitor, particularly for archaeological objects. Initially adopted as a corrosion inhibitor for bare copper [7], BTA has been widely used in metal conservation since the description of its inhibition mechanism in 1963 [8]. Despite the extensive scientific literature published on the subject, conflicting evidence and opinions exist about its effectiveness [9–16]. It has been suggested that BTA efficiency is lower on corroded copper alloys than on bare copper [17]. Also, there are some concerns about its effectiveness on bronze disease since the layer of cupric chloride-BTA complexes formed after treatment would only be superficial and subject to eventual disruption, with reactivation of the corrosion processes underneath it [18]. However, the most controversial argument about the extensive use of BTA is its toxicity. As reported by Cano and Lafuente [17], some authors refer to BTA as an environmental and health hazard product, recommending to handle it with care [2,13], while others describe it as only slightly toxic [7,19]. Thus, in the last decades the interest about alternative, sustainable and harmless products has increased [20].

The bio-based treatment employed here relies on the use of a naturally occurring fungal strain mixed in a hydrogel amended with nutrients. In fact, some fungal species are known for their ability to produce oxalic acid in order to immobilize heavy metals and, for example, detoxify polluted environment [21–23]. Oxalic acid can complex metal ions forming highly insoluble biogenic metal oxalates

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[24,25]. This capability has already been exploited in the field of waste treatment [26–28]. Biogenic oxalic acid production could also be used to turn existing reactive copper corrosion products into more stable and less soluble compounds, while preserving the physical appearance of the artefacts. Indeed, metal oxalates, and more specifically copper oxalates, were already identified on outdoor-exposed bronzes, though not associated with the phenomenon of cyclic corrosion [29]. Instead, compact patinas of an attractive green colour are created on the bronze surface. Moreover, copper oxalates provide a good protection of the surface, given their high degree of insolubility and chemical stability even in an acidic atmosphere [30]. On this basis, an alternative green strategy for the preservation of copper-based artefacts has been proposed. A specific strain of *Beauveria bassiana* isolated from vineyard soils highly contaminated with copper was tested. It has shown the best performance with an almost 100% rate of conversion of copper hydroxysulfates and hydroxychlorides into copper oxalates [31,32]. The newly formed copper oxalates were characterized in-depth to define their properties and to optimize the application procedure on corroded coupons [33–35]. Cross-section examination suggested that the first micrometers of an urban natural patina were completely converted into copper oxalates. The same results were obtained for foundry patinas based on copper nitrates, copper chlorides, copper sulfates and iron nitrates as well [36–38].

We also compared the same bio-based treatment to BTA in terms of conversion of corrosion products and corrosion stabilization of a patina composed of copper chlorides. A weathered copper roof tile was used as the base material to prepare coupons with an artificial atacamite patina. This naturally-corroded samples were selected as they are expected to be more representative of real artefacts than bare copper samples. In fact, the properties of corroded surfaces (roughness, morphology and composition) play a key role in the behaviour of conservation treatments. These characteristics must be taken into account when dealing with application on heritage metal surfaces. Indeed, the corrosion layers are part of the historical value of the objects and must not be removed. However, no generally accepted procedure is yet established to cope with the needs of representative corroded cultural heritage surfaces as available standardised methods only refer to clean metal surfaces [39]. Furthermore, the limited possibilities to test on real artwork require to use non-destructive techniques, as well as the testing of new technologies on corroded coupons as a proxy to real artefacts.

The effect of the bio-based and the BTA treatments on corroded samples were assessed on both the surface and cross-sections of the naturally-corroded samples. A multi-analytical approach using Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Electrochemical Impedance Spectroscopy (EIS) was adopted. The EIS setup enables to perform measurements on both coupons and real artworks allowing for a more straightforward comparison of results in future applications of either treatment.

2. Materials and methods

2.1. Samples production and preparation

Nine samples (2.5 × 2.5 cm) were cut from a naturally aged copper roof tile from Neuchatel, Switzerland. All copper samples exhibited a typical urban natural patina mainly composed of brochantite, a copper hydroxysulfate $Cu_4SO_4(OH)_6$ and cuprite, a cuprous oxide Cu_2O, underneath. The samples' surfaces were washed with acetone in an ultrasound bath with acetone and then dried using compressed air. An artificial patina of copper chlorides was then produced starting from the original patina. A solution with 20 g $Cu(NO_3)_2{\cdot}3H_2O$ (Fluka Germany, purum p.a.) and 20 g NaCl (Panreac Spain, PA-ACS-ISO) in 100 mL deionized water was prepared. The samples were sprayed with this solution and left air dry on a soft cloth. The procedure was repeated twice a day for five consecutive days and finally all samples were rinsed with deionised water [40–42]. Fourier-Transform Infrared Spectroscopy was used to characterize the newly formed artificial patina: it was mostly composed of atacamite, a copper hydroxychloride $Cu_2(OH)_3Cl$ with some traces of brochantite.

The bio-based treatment (biopatina) is based on a gelified culture of the fungal strain S6 of *Beauveria bassiana* [31–38]. To this purpose, the fungus was dispersed in a water solution amended with nutrients and mixed with a solidifying agent. Samples were covered with the obtained gel during 14 days. After treatment the gel was removed and samples were rinsed first with deionized water and then with ethanol (70% w/w solution in deionized water) to remove any fungal residue. The samples were dried using compressed air.

A 3% w/V solution of benzotriazole in ethanol (95% w/w solution in deionized water) was prepared. Two different application protocols were employed. For the first application protocol (BTA1) the corroded samples were fully immersed and left in the solution for 24 h according to protocols commonly used by conservator-restorers on archaeological objects. The second application protocol (BTA2) involved longer immersion time. The corroded samples described above were fully immersed and left in the BTA solution for 14 days (same duration as for the bio-based treatment) to allow for a better comparison of the results. At the end of either treatment, samples were rinsed with ethanol and dried using compressed air. Finally, a group of samples was left untreated as reference for comparison purposes.

All treatments were performed in triplicates.

2.2. Surface characterisation

Before and after treatment, all samples were documented with a scanner HP1110 using a resolution of 600 dpi and setting the white balance with a white paper (Fig. 1). This procedure allowed to evaluate the impact of treatments on the aesthetic appearance of the surface.

2.2.1. Fourier transform infrared spectroscopy (FTIR)

FTIR analyses were performed on the surface of the samples without any preparation using a Nicolet iS5 Thermo Scientific spectrometer with a diamond Attenuated Total Reflectance (ATR) crystal plate (iD5™ ATR accessory). All spectra were acquired in the range 4000–550 cm^{-1}, at a spectral resolution of 4 cm^{-1}. A total of 32 scans were recorded and the resulting interferograms averaged. Data collection and post-run processing were carried out using Omnic™ software.

2.2.2. Scanning electron microscopy (SEM)

Secondary electron images were acquired using a Philips ESEM XL30 FEG scanning electron microscope with a working distance of 10 mm and an acceleration voltage of 20 kV.

2.2.3. Electrochemical impedance spectroscopy (EIS)

EIS measurements were performed with a specially designed contact probe (ST15) which can be used for in-field measurements on artworks [43,44]. A stainless steel pseudo-reference electrode is embedded in PTFE coaxially with a 316 L Stainless Steel Counter Electrode to form a solid contact cell. The nominal area is 1.77 cm^2. The electrolyte used here is a mineral water (electrical conductivity 320μS. cm^{-1}, pH = 7.9) also adopted for field EIS measurements on outdoor bronze artworks as reported in other studies in the conservation field [45]. A commercial cleaning-cloth is soaked with the electrolyte for 120 min, then fixed to the contact cell. The system obtained is then placed on the surface to be measured; the open circuit potential is monitored to check for sufficient stabilisation. The EIS spectra acquisition is started after approximately 30 min when the potential variation over the measurement time is not greater than the applied voltage perturbation. Spectra with 10 points per decade were acquired in potentiostatic mode with 10 mV AC signal level at open circuit potential, in the frequency range 100 KHz - 10 mHz, using a Gamry REF600, with Framework/EIS300 V5.3 software©2007, Gamry Instruments, Inc. In order to properly normalise the acquired data for the measurement area, the wet footprint of the EIS