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Original article

Conservation of ethnographic artefacts: Selective laser ablation of deposits from doum palm fibers

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ABSTRACT

This work approaches the challenging cleaning problem of fragile ancient ethnographic artefact crafted using lignocellulosic fibers, which undergo different and concomitant degrading reactions (oxidation, hydrolysis, depolymerization) over time. Here, the fundamental wavelength and second harmonic of Q-Switched Nd:YAG laser were comparatively tested for the removal of deposits from woven-fibers 'angarêb, which is exhibited at the Africa Hall of the National Geographic Society Museum (Cairo, Egypt). After a careful fiber identification, laser-induced effects were assessed on 'angarêb fibers and fresh, naturally and artificially aged doum palm (*Hyphanae Thebaica*) reference samples by means of stratigraphic examination, UV-induced Vis fluorescence emission, Raman spectroscopy, ESEM-EDX analysis and optical microscopy. Irradiation at 532 nm affected the color appearance and structural integrity of the fibers. Bond-breaking/depolymerization and bleaching occured at this wavelength, due to the significant absorption of lignin/phenolic-carbohydrate and lignin-quinonoid complexes. In contrast, laser irradiation at 1064 nm did not induce any detectable discoloration or structural alteration, either in the short- or long-term diagnostic assessments. The results achieved highlight the possibility of using the latter wavelength for recovering the original surface of soiled ethnographic artefacts made of fragile vegetable fibers, which are otherwise untreatable.

1. Research aim

The maintenance of artefacts crafted using vegetable fibers represents a very difficult task because of the serious deterioration phenomena they typically present. Besides the need of controlled exhibition conditions, the main conservation aspect concerns the removal of soot accumulated through the fibers, whose brittleness makes very armful any chemical or mechanical action. Exogenous materials incorporated during the use of the objects, their storage or museum exhibition affect the legibility of the manufacturing details and accelerate the deterioration processes. Here, we aimed at thoroughly investigating the laser ablation approach for safe contactless cleaning of such a class of ethnographic artefacts. The potential of the laser approach was explored for the first time on samples of a typical Sudanese bed ('angarêb) of 19th century after identifying its constituting fibers. Irradiation tests using the fundamental wavelength and the second harmonic of Nd:YAG laser were carried out on both authentic and prepared samples in order to optimize the treatment and achieve general criteria, which could be exploited for the broad class of fiber objects.

2. Introduction

Ethnographic heritage includes various types of household items crafted using vegetable fibers, such as basketry, matting, ropes, brooms, brushes, and many others. For their production, several grass-like plant species (reeds, palms, cereals, etc.) have been used along the centuries. Parts of the plants (leaves or leaflets, branches, culms, stem) were and, in some cases, still are (living traditions) accurately selected and then processed using different techniques, such as drying, retting, beating, cooking, and combing. Depending on the final use of the object, twisting, spinning, plating and weaving methods were then used to process fibers in form of yarns, strands, and ropes [1–4]. Furthermore, very coarse materials such as striped leaves, stems, or other have often been employed for producing cordage without any specific preparation [5].

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These types of handicraft productions represent a fundamental part of the material culture of population groups of the past, which enrich the ethnographic and anthropological knowledge and must hence be preserved for the future generations. However, considering the relatively highly perishable nature of lignocellulosic materials, the related conservation problems represent a challenging task even when their macroscopic morphology is apparently preserved. Several aspects must be taken into account whenever restoring rare ethnographic findings. The most common deterioration phenomena are related with the presence of moisture, air pollutants, acid and oxidative agents, trace of transition metal ions, long light exposure, and microorganisms (fungi and erosion bacteria) [6–9]. Cellulose and hemicellulose moieties and in lesser extent lignin undergo different and concomitant degrading reactions (oxidation, hydrolysis, depolymerization) leading to brittleness of the fibers and overall fragility of the object, which gets hence easily alterable during cleaning treatments based on wet methods and alkali [10]. It was found that the drying process from an aqueous medium in air alters the cellulose structure irreversibly [11]. Similarly, the cleaning of aged woven-fibers by means of mechanical actions is often time-consuming and invasive, although in the long-term dry cleaning is safer than wet technique for easily hydrolisable carbohydrates.

This picture shows the present conservation problem is substantially open. A suitable cleaning treatment should not involve relevant mechanical actions and be able to remove exogenous materials contributing to the deterioration dynamics (ex. oxidation processes catalyzed by iron ions).

Within this framework, the exploration of laser ablation potential appears very motivated. As shown in many studies (see for example [12] and references therein), this technique, if accurately optimised, can be very selective and self-limiting even when used for uncovering incoherent surface layers. However, works dealing with the study of laser interaction with wooden artefacts are relatively a few [13–16], whilst those regarding archeological plant fibers are decidedly very rare [17]. In both cases, different irradiation conditions were tested, but no detailed information as many as those for de-soiling of paper were reported. It was demonstrated that different wood species (pine, beech, and oak) exhibit an absorptivity higher than 80% in the UV and MIR range, while a very low one at about 1000 nm. As consequence, 1064 nm wavelength was successfully exploited in laser cleaning experiments of wooden artefacts. In turn, minor attention has been dedicated to the influence that pulse length and pulse repetition frequency (prf) has on the ablation mechanism. As general rule, nanosecond pulse lengths and low prf (1–5 Hz) should be preferable when treating natural organic fibers, thus to prevent cumulative heating and consequent discoloration effects (yellowing or bleaching).

In the present work, the potential of nanosecond laser ablation for de-soiling ancient plant fiber artefacts was explored for the first time. The fundamental wavelength and second harmonic of Q-Switched Nd:YAG laser (1064, 532 nm) were comparatively tested in order to remove brown-dark crusts (soot, dirt, aluminum silicates, carbonaceous material) from twisted fiber samples taken from an ancient 'angarêb, a wooden framed bedstead, from the Africa Hall of the National Geographic Society Museum (Cairo, Egypt). Significant efforts were dedicated to identify the fiber type constituting the artefact and to characterize soiling material in order to optimize the irradiation parameters and cleaning procedure. Laser-induced effects at both wavelengths were hence thoroughly investigated through irradiation test of authentic 'angarêb rope fiber and prepared samples. UV-induced Vis fluorescence, Raman spectroscopy, thin sections, ESEM-EDX analysis, and optical microscopy were the main techniques used in order to characterize material composition and assess the laser treatments. Finally, the long-term stability of laser-treated fibers was also investigated.

3. Materials and methods

3.1. The artefact

The wooden framed bedstead 'angarêb (Fig. 1) is a traditional piece of furniture with long history in Sudan dated back to the ancient Kerma culture 1750–1550 BC [18,19]. Nature plant fibers, especially palm leaves, which were easily available and relatively inexpensive, were geometrically woven in order to craft the bedstead.

According to the available information, the low sleeping rest-place with no headboard [20] under study ('angarêb, Cat. No. 351, L∼180cm × W∼80cm × H∼35 cm) belonged to the King Munza of Mangbetu who visited Cairo in 1870. The object is composed of connected wooden frame mounted on four legs with a strong network of two-stranded ropes stretched across the bed frame [18]. In particular, any single string or rope is constituted of two bundles of twisted fibers (2 plies) woven in S-twist shape. Four rope fragments of the mentioned artefact of about 4–6 cm each were set available for the present study by the mentioned Museum.

3.2. Preparation of doum palm samples for systematic irradiation tests

Fresh and natural-dried leaves harvested from mature doum palm (*Hyphaene thebaica, Arecaceae family*) [1] were selected in order to prepare a set of reference samples for systematic tests. Physical and chemical modifications were investigated both on adaxial surface of the leaves, which did not undergo any processing, and on leaves with epidermis stripped off. In detail, the latter were individually hand-washed in distilled water in order to remove most of the mineral particles on the surface and to soften the mineralised tissue. After this pre-treatment, the leaves were scraped off and their fibers manually extracted using a wooden tool. These fibers were then left to dry at room temperature before being cut to the desired length, bundled, placed on a glass slide, and glued at their edges with double-sided adhesive tape. Afterwards, a set of the leaf and fiber samples was artificially aged according to UNI ISO 5630-3 (6 days, 80 °C, RH 65%, absence of light) [7].

This aging treatment was selected in order to induce bond-breaking via hydrolysis mainly to cellulose moieties, although also those of lignin may be affected as well [6,21–23]. The different types of samples prepared are listed in Table 1.

Artificial ageing was also used in order to evaluate long-term side effects after laser irradiation. In this case, slightly softer conditions were used: 6 days, 60 °C, RH = 50%.

3.3. Analytical samples

Transverse and longitudinal thin sections (TS and LS, respectively) were prepared, according to the well-established procedure for treating the present vegetable samples [24]. Twelve single fibers were accurately selected from a rope of the 'angarêb, cut along the transverse direction into small portions (3 mm length) and fixed for 12 h at 4 °C in a solution of 3% (w/v) glutaraldehyde in phosphate buffer at pH 7.1. They were then dehydrated in an ethanol series, and embedded in Epon/Araldite epoxy resin, which was polymerized for 24 h at 60 °C. Afterwards, T and L sections were cut from embedded material, using an ultra sliding microtome.

Surface and cross-section microscopic appearance was also examined with ESEM by using single fibers (3 mm), which were frozen using a Peltier prior to be cut and analyzed. Reference plant

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