Viability of laser cleaning of papyrus: Conservation and scientific assessment

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There has been a growing interest in laser cleaning applications for a variety of organic materials such as paper, parchment, textiles, and leather during the last decade. However, archaeological organic materials, notably papyrus, have rarely been investigated. This contribution examines whether removal of burial encrustation can be justified in view of its short-term and long-term effects on the substrate. To examine this, tests using mock objects have been performed. Using artificially soiled and archaeological papyrus samples, optimization of laser cleaning parameters using a picosecond laser (1064 nm, various operating conditions) was attempted. Optimization was based on colorimetry, optical microscopy, scanning electron microscopy, Fourier transform infrared spectroscopy, and cellulose degree of polymerization data, both before and after accelerated degradation. In papyrus, there is no clear damage threshold, and substrate degradation can always be observed and is comparable in treated (cleaned) and untreated (soiled) objects. Therefore, the decision on whether to clean papyrus using lasers is predominantly based on aesthetic and treatability (e.g. need for consolidation) criteria.

Keywords: Papyrus, Paper, Burial dirt, Picosecond, Colorimetry, Degree of polymerization, Optimization

Introduction
The interest in laser cleaning applications for a variety of organic heritage and archaeological materials such as parchment, leather, paper, and basketry has grown considerably in the last decade (Arif et al., 2013; Andreotti et al., 2007; Elliott et al., 2007; Elnaggar et al., 2011). However, to our knowledge, this is the first comprehensive evaluation of the potential of laser cleaning intervention for papyrus. The justification of cleaning must be carefully considered and should be based on the assessment of the aesthetic legibility of papyrus artefacts, the potential need for consolidation which may require the prior removal of surface dirt. In addition, recent research has demonstrated the influence of dirt on cellulose degradation, which suggests that cleaning is an essential step for preventive conservation (Bartl et al., 2015). Since the concept of ‘damage threshold’ depends on the method of observation, it is crucial to justify and optimize the cleaning process using a set of conservation and scientific criteria.

Papyrus sheets are made of the fibrous material found within the stems of the aquatic grass-like plant Cyperus papyrus L. As writing material, it was light, thin, and durable. However, in ancient Egypt, papyrus was also used for other purposes: cords, basketry, boats, and sails (Parkinson et al., 1995). The use of papyrus was continuous throughout the Graeco-Roman Egypt, the byzantine, and early Islamic period (Thomas, 1988; Lucas, 2003). Papyrus consists of 97% cellulose, hemi-cellulose and lignin, and 3% proteinaceous materials (Leach & Tait, 2009).

Since papyrus sheets are not a paper-like material (i.e. sheets are not cast from a suspension of fibres but rather woven from ribbons cut directly from plant stems), they have a rough surface. The content of lignin can be as high as 12–34% (Parkinson et al., 1995; Owen & Danzing, 1993) – as an amorphous polymeric substance lignin is particularly unstable and plays an important role in the properties and the degradation of cellulose materials (Kronkright,
1990; Katuscak et al., 2006). Similar to other excavated organic archaeological materials, papyrus can be contaminated with dirt and salt particles, which may appear as a thin encrustation (Leach & Tait, 2009). This crust prevents the application of consolidation interventions and could have a negative effect on the object in terms of its chemical stability and mechanical strength.

Removal of encrustation is a challenging intervention, especially if the object is fragile. Traditional mechanical and chemical cleaning methods may cause disruption of fibres or chemical change, thus accelerating the degradation of cellulose (Kronkright, 1990; Rouchon-Quillet, 2003). In this regard, laser cleaning could offer an advantage due to its selectivity, precision and minimal material handling. However, it is well known that laser cleaning of cellulosic materials may also lead to photothermal and photochemical degradation such as yellowing, chain scission, and cross-linking (Kautek et al., 1998; Kolar et al., 2000, 2002, 2003; Vergès-Belmin & Dignard, 2003). For the removal of dust on paper, past studies recommended the use of IR and visible lasers over ultraviolet lasers with radiation of higher energy, in order to avoid photo-oxidation of cellulose and bond scission (Kronkright, 1990; Kolar et al., 2000). However, even at wavelengths longer than 340 nm, degradation could still take place.

In this study, we used a picosecond (ps) laser which was expected to reduce thermal effects, which have been shown to lead to yellowing (Strlič et al., 2003). The recent development of industrial laser applications with ultrafast pulses led to minimization of thermal side effects (Stuart et al., 1995) and satisfactory results have been obtained for cleaning of metal artworks (Barcikowski et al., 2006; Rode et al., 2006). In addition, ps pulses lead to lower volumes of ablated material from the object surface per pulse, which enables high-precision cleaning.

The aim of this work is to examine whether laser removal of burial encrustation on papyrus can be justified. In the process of optimization, changes in chemical (immediate and long term) and mechanical properties were weighed against the cleaning effect. This work thus aims to assess laser removal of soiling (artificial and authentic) by developing an understanding of the thermal effects of laser irradiation (resulting in bleaching or yellowing or any other chemical change which might accelerate material degradation).

Materials and methods

Model samples and accelerated degradation

To examine the effect of soiling on degradation and evaluate if its removal has a beneficial effect on the stability of cellulosic materials, purified cellulose samples (lignin-free Whatman paper No. 1, WH, DP 2270) and model papyrus (DP 1547) sheets were surface-soiled with the following:

- ASHRAE (52/76) synthetic dust (consisting of 72% silica and 23% carbon black, oxides, and fibres), supplied by Particle Technology Ltd (Hatton), UK, referred to as ‘Dust’, containing Fe, Si, Ca, and traces of Al, P, S, Cl, and Na.
- Authentic well-characteristic tomb dirt (containing Ca, Si, Fe and traces of Al, P, Mg, Na, and Cl) collected from the archaeological papyrus rope object, referred to as ‘Dirt’.

Model papyrus samples were purchased from the ‘Pharaonic Village’, Giza, Egypt, produced in a manufacturing process similar to archaeological papyrus.

Thin layers of dust and dirt were applied to the paper samples using a dry brush. In order to approve the adhesion onto the smoother papyrus surface, dust and dirt were wetted with distilled water and brushed onto the surface. Accelerated degradation of the soiled samples was performed in a Vötsch VC3 climate chamber (Reiskirchen-Lindenstruth) for 28 days at 70°C and 50% RH.

Case study object

Fragments of an ancient papyrus rope, ca. 3100 BCE, from the Agriculture Museum in Giza, Egypt, excavated from Saqqara, Egypt, Object number 4383, Fig. 1, were kindly supplied for this study by the Museum. The thick rope is made of papyrus stalks, is of brown colour with a greyish tinge due to the accumulation of a thin crust on the surface. Visual and microscopic investigations indicated that the rope had no decorative marks or pigment applications. The object is in a poor state: dry, wrinkled, loose, brittle, and soiled. The rope is twisted due to its function and use, which makes cleaning difficult. The grey crust of compact burial dirt is strongly adhered to most surfaces of the substrate.

Laser cleaning

Laser cleaning was performed at the Faculty of Engineering, Liverpool University, UK, using a custom-made Nd:YAG seeded regenerative amplifier ps laser (High Q, Photonic Solutions, Edinburgh) with a repetition rate of 10 kHz with the output wave-length of 1064 nm and a temporal pulse length of 10 ps. Irradiation of the samples was controlled using a computerized system controlling the size and shape of the scanned areas, pauses between pulses and the scanning speed. The tests were carried out using fluences between 0.62 and 6.37 J cm\(^{-2}\), power output 100 mW; number of scans 1–20, traverse speed 300–825 mm s\(^{-1}\); constant laser spot size: 30 μm; constant hatch spacing: 0.03 mm and 10 kHz repetition rate.
The laser beam output was fixed above a sample mounted on an A3-axis motion-control system (Aerotech, Ramsdell) in conjunction with NView MMI software to manipulate samples and select the size of the scanning area with an automatic distance detection and adjustment of the laser beam focus. The experimental set-up of the laser systems has been reported for conservation purposes previously (Pouli et al., 2005; Watkins et al., 2009; Kono et al., 2013).

**Microscopy and SEM-EDX**

A stereomicroscope (Olympus SZX7, Shinjuku) was used for microscopic examination. We also used a scanning electron microscope (SEM) Carl Zeiss EVO LS15 (Jena) coupled with an energy dispersive X-ray (EDX) detector (Oxford instruments X-Max) with no sample preparation or coating. A portable electron-scanning microscope SEM (FEI Phenom, Netherlands) was also used with no sample coating.

**Determination of degree of polymerization**

Viscometry was used in this study to determine the degree of polymerization (DP) of papyrus and paper. We developed a new method of sample preparation since papyrus, in comparison to paper, consists of natural fibres which had to be mechanically broken down before dissolution. The fibres were separated manually and mixed with drops of distilled water and ground mechanically prior to dissolution.

The standard viscometric method was used (ISO 5351/1:1981). DP was calculated from intrinsic viscosity, \([\eta]\), using the Mark–Houwink–Sakurada equation: \(DP^{0.85} = 1.1[\eta]\) (Evans & Wallis, 1987).

**Colorimetry**

Colorimetric measurements were carried out in accordance with the Commission Internationale de l’Eclaraige (CIE) Lab colour system (1976) using a spectrodensitometer (X-Rite 530) to measure colour changes on the L* scale (Luminosity), b* scale (yellow/blue colour) and a* scale (red/green colour). In this paper, an increase in the L* value will be used to describe the efficiency of laser removal of dust/dirt while an increased b* will be used to denote undesirable yellowing. Seven measurements were averaged to obtain one data point.

**FTIR**

Fourier transform infrared spectroscopy (FTIR) was carried out using a Thermo Nicolet iS10 FT-IR spectrometer in reflectance mode using an attenuated total reflectance (ATR) slide-on accessory with a diamond crystal, spectral range 4000–400 cm\(^{-1}\) and resolution 4 cm\(^{-1}\).
Results and discussion

Investigation of the rope papyrus

SEM-EDX microscopic and chemical investigations of the papyrus rope (Fig. 2) indicated that the burial dust consisted of sodium aluminium silicates and chlorides as the main elements of dirt, possibly containing calcite and gypsum, with some content of iron. Iron is known to strongly promote oxidative degradation of cellulosic materials (Selih et al., 2007), which is why this result was of particular interest. The microscopic investigation shows how deeply dirt particles penetrated into the surface of degraded papyrus, indicating its low mechanical resistance, demonstrating the potential of dirt to contribute to mechanical degradation of the fragile material. In the next section, we will investigate whether dust and dirt also contribute to long-term chemical degradation of cellulose.

Effect of dust and dirt on cellulose

The application of dust on paper led to a reduction in L* from 94.9 to 47.8, and to 68.4 with the application of dirt. The b* value was reduced from 2.2 to −0.3 after applying dust and increased to 20.6 after applying dirt due to its natural colour. The L* value of papyrus was reduced after application of dust from 77.6 to 43.2 while the b* value was reduced from 23.9 to 7.6.

After the application of dust and dirt on paper and papyrus, the samples were exposed to accelerated degradation in order to ascertain whether soiling affects the stability of these materials. Viscometric analysis was performed to determine the degree of DP of cellulose (Table 1). The data show that the DP of WH paper decreased by 13% during degradation, while this decrease was 18% for WH with dust and 28% for paper with dirt. The increased DP of papyrus after accelerated degradation is difficult to explain and more research is necessary to ascertain whether this was due to an experimental error or natural inhomogeneity of the material. Our results are similar to those reported by Bartl et al. Dust clearly negatively affects the degradation of papyrus.

Table 1 DP of cellulose in paper and papyrus after soiling and accelerated degradation (relative to non-degraded sample)

<table>
<thead>
<tr>
<th>Sample</th>
<th>DP (%change)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-degraded WH</td>
<td>2272</td>
</tr>
<tr>
<td>Degraded WH</td>
<td>1987 (−13%)</td>
</tr>
<tr>
<td>Degraded WH-soiled with dust</td>
<td>1917 (−18%)</td>
</tr>
<tr>
<td>Degraded WH-soiled with dirt</td>
<td>1630 (−39%)</td>
</tr>
<tr>
<td>Non-degraded papyrus</td>
<td>1547</td>
</tr>
<tr>
<td>Degraded papyrus</td>
<td>1768 (14%)</td>
</tr>
<tr>
<td>Degraded papyrus-soiled with dust</td>
<td>1392 (−11%)</td>
</tr>
</tbody>
</table>

The data in Table 2 demonstrate that dust and dirt significantly contribute to the degradation of cellulosic supports. Thus, in conjunction with microscopic analysis of the case study object, showing the fragility of the surface and the potential contribution of particles to mechanical degradation of the surface, there is a clear motivation for exploring laser cleaning for the papyrus rope object. Optimization of the process proceeded by testing the cleaning procedure on pure cellulose and model papyrus first.

ps-pulsed laser cleaning of paper

In the process of optimization, we tested a number of operating parameters, always using L* as an indicator of the efficiency of cleaning, and an increase in b* as an indication of chemical degradation of the support as a consequence of laser cleaning, while images in Fig. 3 show the progress of cleaning using optical microscopy and SEM.

The data in Figs. 3 and 4 show that it is not possible to entirely remove soiling from WH with any combination of fluence and number of scans, although 3.18 J cm⁻² and 6–10 scans, and 1.91 J cm⁻² 7–20 scans came very close to L* of the degraded and non-soiled WH sample. It is evident that with higher efficiency of removal of dust, yellowing increases as well – this is a well-known phenomenon and has been extensively explored previously (Strlić et al., 2003) with nanosecond-pulsed lasers. However, there seems to be slightly less pronounced yellowing at 3.18 J cm⁻² than at 1.91 J cm⁻².

The colorimetric measurements following ps laser cleaning of pure cellulose soiled with dust indicate that cleaning is never entirely successful. Interestingly though, SEM images indicate no noticeable morphological change of paper fibres.

There is, however, evidence of chemical change, as viscometric determinations of DP following laser cleaning at a fluence of 1.91 J cm⁻² using 20 scans showed an increased DP of cellulose of 2080, comparing to non-cleaned and non-soiled degraded sample (DP = 1920). This indicates that ps laser cleaning of soiled cellulose might lead to cross-linking. It is

Table 2 L* and b* values of model samples made of Whatman (WH) paper and papyrus

<table>
<thead>
<tr>
<th>Sample</th>
<th>L*</th>
<th>b*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-degraded WH</td>
<td>95.2</td>
<td>1.5</td>
</tr>
<tr>
<td>Degraded WH</td>
<td>94.9</td>
<td>2.2</td>
</tr>
<tr>
<td>Degraded WH-soiled with dust</td>
<td>47.8</td>
<td>−0.3</td>
</tr>
<tr>
<td>Degraded WH-soiled with dirt</td>
<td>68.4</td>
<td>20.6</td>
</tr>
<tr>
<td>Non-degraded papyrus</td>
<td>81.7</td>
<td>20.6</td>
</tr>
<tr>
<td>Degraded papyrus</td>
<td>77.6</td>
<td>23.9</td>
</tr>
<tr>
<td>Degraded papyrus-soiled with dust</td>
<td>43.2</td>
<td>7.6</td>
</tr>
</tbody>
</table>
known that these chemical changes affect the rate of future degradation of cellulose (Kolar et al., 2000).

Soiling with dirt led to slightly different results (Figs. 5 and 6). The soiled sample has a significantly high $b^*$ of 20.6 after degradation, in comparison with the non-soiled but degraded sample ($b^* = 2.2$), which is due to the chemical composition of natural dirt. Due to the colour of dirt itself, any yellowing during removal will therefore be very difficult to interpret due to the two competing processes: removal of yellow dirt and yellowing of the substrate.

Laser cleaning of WH soiled with dirt showed that after the procedure, $L^*$ of the treated sample is very similar to the degraded, but non-soiled paper. Furthermore, laser ablation of the dirt particles led to a reduction of $b^*$, or a decrease in the yellow tinge imparted by the presence of dirt. A fluence of $3.18 \text{ Jcm}^{-2}$ and 20 scans appear to be the most favourable combination for removal of natural dirt from WH paper: luminosity is greatly improved ($L^* = 85$), and the yellow component was reduced ($b^* = 17.6$) compared to the soiled and degraded sample. DP of this sample was slightly higher ($\text{DP} = 1660$). Removal of authentic dirt from WH requires a higher number of repetitions (number of scans) at the same fluence, when compared to dust.

It is difficult to speculate about the reasons for this observation, although the differences in optical properties of silica-based dirt and carbon-based dust must be high. Tests on WH demonstrate that ps laser removal of dust and dirt from pure cellulose depends on the nature of soiling, we investigated cleaning of papyrus, which – as a lignin-containing cellulosic material – is expected to behave differently (Strlić et al., 2003).

**Laser cleaning of model papyrus**

Initial laser cleaning tests indicated that at low fluence ($1.91 \text{ Jcm}^{-2}$) and even high number of scans (10 scans), there was no significant removal of soiling. In Fig. 7, we examine the effect of dust removal at higher fluences. It is difficult to optimize the cleaning process as there is always some observable surface damage on papyrus. In Fig. 8 D–F, we see a satisfactory cleaning result. Since at lower fluences there was no measurable cleaning result, we attempted to use higher fluences: with $3.18 \text{ Jcm}^{-2}$ and three scans, $L^*$ after cleaning improved, from 43.2 to 71.3.

Changes in yellowness are of interest as it seems that (as with other lignocellulosic materials) there are competing processes – both bleaching and yellowing (Fig. 7). At high fluences ($6.37 \text{ Jcm}^{-2}$), but also at lower fluences ($3.18 \text{ Jcm}^{-2}$) and higher number of repetitions, bleaching is observed (reduction in $b^*$) compared with the non-soiled and degraded sample (Fig. 7). For the model papyrus, the most favourable

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**Figure 3** Optical microscopic images (A–D) and SEM micrographs (E–H) demonstrating the progress of laser cleaning of dust from WH with uncleaned areas are on the left of images (A–D) and SEM images show cleaned area (E–H): (A) and (E) $3.18 \text{ Jcm}^{-2}$, one scan; (B) and (F) $3.18 \text{ Jcm}^{-2}$, five scans; (C) and (G) $3.18 \text{ Jcm}^{-2}$, 10 scans; (D) and (H) 1.91 $\text{ Jcm}^{-2}$, 20 scans.

**Figure 4** Colorimetric measurements ($L^*/b^*$) of Whatman paper (degraded clean, degraded soiled with dust, and laser cleaned) using different fluences and number of scans ($r$).
result ($L^* 78.5, b^* 21.8$) was achieved using a fluence of $3.18 \text{ J cm}^{-2}$ and five scans, as this compares well with the colour data for the degraded and non-soiled papyrus ($L^* 77.6, b^* 23.9$; Figs. 8 and 9). ATR-FTIR of papyrus before and after laser cleaning of dust ($3.18 \text{ J cm}^{-2}$ and five scans) indicates very small differences – $0.04 \text{ AU}$ is barely significant. The carbonyl region at approximately $1700 \text{ cm}^{-1}$ shows no appreciable degradation, and very small increase of the band at approximately $1000 \text{ cm}^{-1}$ ($-\text{C}-\text{O}$ stretching) could signify some dehydration (removal of water and formation of ether bonds), which is consistent with the observed cross-linking in WH.

The results show that soiling cannot be entirely removed from pure cellulose ($L^*$ after cleaning never quite reaches the same value as for the non-soiled and degraded sample), and there is always some chemical degradation (as evident from changes in $b^*$). However, there appears to be no mechanical damage to the surface. Soiling can be removed from papyrus surface; however, this is accompanied by mechanical damage and in some cases by bleaching, as observed previously for ligneous materials (Strlič et al., 2003). Reactions of lignin and cellulose to laser cleaning and consequential colour changes are two competing processes.
However, as shown with pure cellulose samples, natural burial dirt tends to have a negative effect on the long-term stability of cellulosic materials (Bartl et al., 2015). From the conservation point of view, it is therefore a question whether degradation caused during laser cleaning compares favourably or not with the degradation caused by soiling in the long term. Since no mechanical or chemical cleaning treatment of fragile papyrus is safe for its mechanical integrity, laser cleaning appears to be a viable option.

**Laser cleaning of the archaeological papyrus**

Laser cleaning tests for removal of burial crust from the archaeological papyrus rope were only started after extensive optimization and analysis on model samples. Microscopic investigation (see Fig. 9) and chemical analysis of the papyrus surfaces before and after laser tests were performed to evaluate the cleaning. The results indicate that laser cleaning using a fluence of 1.91 Jcm \(^{-2}\) and 10 scans removed the burial crust safely without damaging the papyrus fibres, while 12 scans at the same fluence damaged the papyrus. Also, a fluence of 3.18 Jcm \(^{-2}\) and three scans was able to provide the same satisfactory cleaning result, comparing to 1.91 Jcm \(^{-2}\) and 10 scans. Damage was also observed at fluences greater than 3.18 Jcm \(^{-2}\).

SEM-EDX (scanning mode) analysis of the archaeological papyrus surfaces before and after laser tests.
indicates that the burial dirt particles were removed. No significant difference was detected in the subtracted ATR-FTIR spectrum between the laser cleaned and non-cleaned archaeological papyrus.

Conclusion
Using contemporary cellulosic samples we have shown that dust as well as dirt can be cleaned using a ps-pulsed laser. However, we encountered the same drawbacks as previously shown for nanosecond-pulsed laser cleaning: chemical degradation as evidenced by yellowing, and measurements of DP. With papyrus having a lignin content of up to 34%, its behaviour during pulsed laser cleaning was similar to lignin-containing paper as described in the literature, with competing chemical processes taking place, such as bleaching of lignin and yellowing of cellulose. At high fluences, or exposure to a higher number of repetitions, significant damage of the surface of papyrus is observed. After the extensive tests performed on model samples, limited testing was carried out on a fragment of archaeological papyrus.

Results demonstrate that the window where ps laser cleaning can be performed safely on papyrus is difficult to identify. The operation of ps cleaning systems available today with only few repetitions is a further challenge. Chemical changes induced by ps laser cleaning at 1064 nm, both immediate and long term also require further investigation.

The decision on whether to clean dust from archaeological naturally aged papyrus should be based on aesthetic and ethical considerations. There is an argument to clean archaeological papyrus to improve its chemical and mechanical stability: results from this work demonstrate that authentic archaeological dirt promotes the long-term chemical degradation of cellulosic materials and contributes to surface abrasion of fragile and dry surfaces, although it is recognized that the potential degradation effect of dust and dirt is small in comparison with the effect of the storage environment. From the ethical standpoint, the argument for cleaning is less clear; while archaeological dirt is contextual, display of artefacts may necessitate cleaning of superficial dust. Removal of dust should be attempted without the removal of burial dirt – a challenge as the optical properties of dust and dirt are similar. Should cleaning be attempted, the fragility of archaeological material may exclude the use of mechanical or chemical cleaning methods, which makes laser cleaning in the ps regime an alternative to other cleaning regimes with different pulse durations and fluences.

References


