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Original article

Femtosecond laser cleaning of historical paper with sizing

Tansu Ersoy[a], Tugba Tunay[a], Mehmet Uğuryol[b], Gurcan Mavili[c], Selcuk Akturk[a,*]

[a] Department of Physics, Istanbul Technical University, 34469 Maslak, İstanbul, Turkey
[b] Yıldız Technical University, Vocational School of National Palaces and Historical Buildings, 34349 Besiktaş, İstanbul, Turkey
[c] Mimar Sinan University, Department of Traditional Turkish Arts, 34427 Fındıklı, İstanbul, Turkey

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ABSTRACT

Lasers have served as cleaning tools for historical objects and artworks for about 40 years. In many cases, superior results of laser cleaning were achieved with respect to traditional methods. In this technique, contaminations on the surface of the object are ablated by laser irradiation. In order to apply laser cleaning method to fragile materials such as paper made of cellulose or parchment, heat deposition to the bulk should be minimal, to prevent damage. In this work, it is demonstrated that laser pulses with femtosecond (fs) duration can exhibit non-thermal ablation of contaminants on paper samples. In particular, laser cleaning studies are concentrated on paper samples with sizing. Fs laser cleaning is performed on artificially soiled and aged samples, as well as on historical ones. The laser used in the experiments has pulse duration of 550 fs and 1030 nm center wavelength. The fluence of the laser is varied and the post-cleaning statuses of samples are investigated. The analyses are color changes, fiber integrity, chemical composition changes and mechanical strengths. These results show that fs lasers can be very efficient in cleaning paper samples, yielding minimal discoloration and no damage to fibers distinguishable on microscopic examination. The presence of sizing also provides further protection against possible side effects.

1. Research aims

We present our experimental results on cleaning of historical paper samples through femtosecond laser ablation. We mainly concentrate on laser cleaning of paper with sizing. Sizing (*ahar*) was used extensively in Islamic handwritten documents and it can also be found in other cultures. It is usually made of egg-white and wheat starch, and applied on paper surfaces for several purposes such as improving mechanical strength, preventing the excessive absorption of ink not to spread on the paper, and providing aesthetical glare. Historical documents and artwork made of paper can have various types of surface contaminants, including degraded glues, ink stains, airborne particles and biological agents. We demonstrate that, the non-thermal ablation mechanism specific to femtosecond lasers can become very powerful in removing surface contaminants, causing minimal or no damage to the paper integrity. We evaluated color changes, chemical composition, fiber integrity and mechanical strength after laser cleaning. The presence of sizing serves as a protective layer during the process. Our results show that femtosecond laser cleaning can yield successful cleaning in papers especially those with sizing.

2. Introduction

Conservation of cultural heritage requires eliminating existing damage and preventing future deterioration as efficiently as possible. Since historical artifacts exhibit a vast variety of materials, shapes, surface textures and production techniques, applicability of any conservation method should be carefully evaluated and tested for each type.

Removal of contamination on artifacts without altering the substrate and authenticity is an essential part of the conservation process. In this regard, cleaning of historical artwork by laser ablation has been a particularly attractive alternative method for the last couple decades [1]. It has been applied to many different historical materials such as stone, paintings, sculptures, textiles, etc. [2]. Laser cleaning is based on selective ablation of contaminants from surfaces; and it has particular advantages as it is non-contact and chemical-free. Lasers have several controllable parameters such as wavelength, pulse duration and power. In general, these parameters can be adjusted to efficiently remove dirt layers with minimal damage to the artifacts. For example, early works indicated that Nd:YAG laser at 1064 nm wavelength may cause yellowing on marble, whereas its second harmonic (at

* Corresponding author.
E-mail address: selcuk.akturk@itu.edu.tr (S. Akturk).

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532 nm) causes no discoloration [3]. However, further and more detailed studies on yellowing have shown that it may result from various sources, including the presence of original yellow layers underneath [4].

To date, Nd:YAG lasers have been used for cleaning of stone monuments in numerous conservation projects [5,6], as mechanical strength and optical properties of stones provide advantages. The large optical absorption contrast between light colored original surfaces and black encrustations brings about "self-limiting" feature of laser cleaning, where the laser fluence is kept in the large gap between the ablation thresholds of these two layers [7].

In laser cleaning of more fragile works such as paintings, the varnish layers provide advantages in that they have very limited penetration depth for ultraviolet (UV) light and for particular infrared (IR) bands, thereby preventing accidental exposure of pigments to laser irradiation [8,9].

Paper and related artifacts also constitute a class of fragile materials. As many conventional techniques involving mechanical or chemical processes used for cleaning historical paper have certain drawbacks and limitations [10], there have also been studies for investigation of cleaning parchment and paper artifacts with lasers. In one of the earliest works, Kautek et al. reported laser cleaning results on coated collagen and cellulose paper [11]. Excimer laser (308 nm wavelength) was successful in removing contaminants from ancient parchment. In the same work, laser induced breakdown spectroscopy (LIBS) and laser induced fluorescence (LIF) were also evaluated as feedback mechanisms and the latter was found to be more effective. The LIF measurements use the details of the emission bands and thereby allow monitoring of fiber damage. More extensive investigations of interaction of UV laser with the parchment indicate that chemical conversion can take place in addition to ablation and close monitoring is necessary to avoid damage to collagens [12], which can clearly show up in scanning electron microscope (SEM) images [13]. Another work in which effects of laser fluence and wavelength on molecular structures of parchment were evaluated, indicated that UV wavelengths cause reduction of hydrothermal stability and molecular integrity [14]. In other works, particular stains were effectively removed from historical cellulose paper with no sign of fiber damage with the aid of a visible laser (Nd:YAG laser at 532 nm) and simultaneous LIF measurements [15,16]. However, reduction of tensile strength of artificially aged and inked paper after laser cleaning was reported in PARELA project, and this was attributed to hornification (irreversible hydrogen bonding resulting into lower flexibility and increased brittleness) occurring as a result of thermal effect of nanosecond laser ablation on fibers and fibrils [17].

Recently, material removal through femtosecond (fs) laser ablation started to be applied to paper cleaning. Fs laser ablation is well-known to have highest-quality and minimal side effects, by virtue of the extremely short pulse durations, leaving no time for heat diffusion during the absorption of light [18,19]. Even for materials of highest thermal conductivities (e.g. metals), lattice heating time (time needed for the laser-heated electrons to transfer their energies to the ions) is of the order ~100 ps [19]. For dielectrics, these times are much longer [20]. In all cases, the duration of the fs laser pulses is orders of magnitude shorter. Therefore, practically no heat diffusion takes place during absorption of laser light, thereby minimizing heat-related side effects. Furthermore, in the case of dielectrics, the laser light is absorbed through nonlinear-optical processes, which further improve the spatial resolution of the ablation process beyond the diffraction limit [21]. These advantages are promising for application of fs lasers to cleaning of fragile artworks such as paper. However, since these lasers are typically more costly and they require a deeper level of expertise, few number of applications in paper cleaning are present in the literature. In one of them, the lack of heat transport to the bulk of the material during fs laser ablation is exploited for cleaning of oxide and rust layers in exposed aluminum, aged brass samples [22]. Moreover, outer layers of extraneous deposits and inner layers of copper corrosion products were selectively removed from historical bronze. Fs pulses with ultraviolet wavelengths are used in cleaning of painting varnishes and the high-spatial-resolution nature of the process mentioned above proved to improve the control on induced modifications [2,23,24]. Other materials used in fs laser cleaning research include silver threads (used in fabrics), bronze monuments [25] and ornamental granite [26].

Walczak et al. compared the cleaning performance of a fs laser with Nd:YAG laser on calfskin parchments [27]. They observed that the fs laser ablation process does not yield damage to collagen fibers, yet can cause photodegradation. More recently, Pentzien et al. presented comparative study involving nanosecond, picosecond and femtosecond pulses [28]. They evaluated the cleaning performance on different types of artificially soiled paper. They observed best colorimetric results (minimum color change) with the nanosecond laser. On the other hand, for the same laser fluences, cleaning was most effective with the fs laser.

In this work, we present our detailed experimental studies on fs laser cleaning of paper samples with sizing. Sizing is very commonly used in traditional Islamic handwritings. It is made of egg white and different kinds of starches, and serves several purposes such as improving mechanical strength, enabling to correct small errors by preventing ink absorption and obtaining better aesthetic view. Although it is a part of the artifact, it can be partially removed and sometimes renewed during certain conservation treatments [10], as in the case of the varnish in the oil paintings. In our experiments, sizing provided a significant advantage in laser cleaning of the zones without paint and ink. We show that the non-thermal ablation of contaminants by fs laser is very effective with the presence of sizing that serves as a protective layer. To the best of our knowledge, this is the first report in literature on the study of laser cleaning of paper in Islamic manuscripts with sizing (*ahar*).

In our experiments, we evaluated the effects of various laser parameters such as average power, scanning speed and scanning pitch. For post-process evaluation, we investigated color changes, chemical composition, fiber integrity and mechanical strength. The effect of laser cleaning on mechanical strength of paper is an important parameter in terms of proper conservation, yet very few studies were performed previously [29]. Similar strength tests have recently been employed by Taarnskov et al. to characterize the strengths of laser-cleaned silk threads [25]. Our results show that removal of sizing inevitably compromises paper strength, yet with adjustment of laser power, this effect can be minimized.

3. Materials and methods

3.1. Preparation of paper samples

In the first stage of experiments, we used different types of non-historical paper samples. The papers were acid-free and aimed for calligraphy. To be able to make comparative studies, we used new papers with and without sizing, as well as hand-dyed (without sizing). We also used samples from approximately 10 years old paper with sizing. All these paper samples are artificially contaminated and aged under the same conditions. For contamination, we used commercial starch-based stick glue (Pritt-Henkel) covered with graphite pencil powder and blue crayon stains. For aging process, we aimed to simulate aging occurring naturally. Therefore, we neither preferred elevated temperatures (e.g. 160 °C) that cause thermal degradation which does not take

Table 1
List of paper types used in fs laser cleaning experiments.

Label	Sizing type	Origin
Artificially contaminated		
A1	Egg white and starch	Artificially aged
A2	None	Artificially aged
A3	Hand-dye	Artificially aged
A4	Egg white and starch	~10 years old
Historical		
B1	Starch	XVII. c
B2	Starch	XVIII. c (first half)
B3	Starch	XVIII. c (first half)

place in moderate conditions, nor use dry-heating (low relative humidity) up to lower temperatures that allows hornification but does not promote hydrolytic degradation because of the absence of moisture [30]. To achieve our purpose, we established 90 °C and 50% relative humidity environment recommended in standard test methods such as ASTM D 4714 and TAPPI T 544 cm-08, and the papers were exposed to this environment for 13 days.

In the second experimental stage, we investigated laser cleaning on three different historical papers belonging to different periods between 17th and 18th centuries. All historical samples had original starch based sizing. The properties of paper samples are summarized in Table 1, where artificial samples are labeled as A1-A4 and historical ones as B1-B3.

3.2. Cleaning experiments

The experimental layout we use for cleaning experiments is shown in Fig. 1. We use Yb:Glass femtosecond laser amplifier system working at a wavelength of 1030 nm. The repetition rate of pulses is 1 kHz, and the pulse duration is 550 fs. The laser beam is brought to a line focus on the sample surface by a cylindrical lens of focal length 25 mm. At the line focus, the beam spot sizes (full-width at half maximum) are approximately 1 mm and 10 μm in the two transverse directions. The sample is placed on a three axis motorized translation stage. By raster scanning the sample under laser illumination, we clean $10 \times 10\,mm^2$ areas. Since the laser beam has a Gaussian transverse profile in the focus, there should be some overlap between consecutive scans. The scanning speed also affects the cleaning experiments; fast scans yield incomplete removal of dirt and very slow scans cause damage to paper. After optimization experiments, we determined the optimal scan pitch to be 0.5 mm and speed 1 mm/s. We use these parameters for all experimental results presented below. For laser ablation process, the main parameter of concern is the laser fluence (energy per unit area) at the focus. To control the fluence in our experiments, we adjust laser pulse energy, typically in the range of 80 to 230 μJ (corresponding to 80 to 230 mW average powers), by using a polarizer and a waveplate.

4. Characterization and experimental results

4.1. Color measurements

One of the most critical parameters in assessing the performance of artifact cleaning is the color change. After the laser cleaning experiments, we measured relative color of the cleaned and non-processed regions of all paper samples using reflected-color measurement spectrophotometer (Hunterlab MiniScan EZ). We used CIE-$L^*a^*b^*$ color system in our measurements. $L^*a^*b^*$ color space is a three dimensional rectangular space for quantization of color and color changes. L axis represents lightness (0 = black and 100 = white). Positive values of a-axis are red and negative ones are green; positive values of b-axis are yellow and negative ones are blue. Color measurements of untreated areas were carried out three times on different regions of each paper and the measured values were averaged to obtain reference values (L_R^*, a_R^*, b_R^*). Relative color changes are determined from $\Delta L^* = L^* - L_R^*$, $\Delta a^* = a^* - a_R^*$ and $\Delta b^* = b^* - b_R^*$ values.

Variations of ΔL^*, Δa^*, Δb^* values with the laser power are shown in Fig. 2 (for artificially contaminated and aged samples) and Fig. 3 (for historical samples). In almost all cases, the brightness of the sample increases, as a result of dirt removal, as expected. However, variations in other colors are mostly minimal, especially for low laser powers. Further discussions on color measurements are included in the discussion section below.

4.2. Microscopy and imaging

We inspected the surface modification of the samples by optical (Nikon, Eclipse, LV150L) and scanning electron microscopy (SEM, Carl Zeiss, EVO LS 10). We also took close-up photographs from the cleaned historical samples.

Optical microscopy images of some of the cleaned samples (A1 and A4) are shown in Fig. 4. One can observe that the laser ablation process selectively removes the superficial dirt layers and causes no burning or visible fiber damage on the paper. Black regions on these images are the remains from the glue layer contaminated with graphite powder. It can be observed that higher laser powers are more efficient in complete removal of the dirt.

For a more detailed investigation of fiber structure, we performed SEM analysis. SEM micrographs of historical papers (B1) are shown in Fig. 5. In this figure, images of untreated areas and regions cleaned with two different laser powers are shown. We observe that, for high average powers, along with the dirt layer, the laser ablation process also partially removes the sizing (Fig. 5b). However, even in this case, there is no observable damage on cellulose fibers, which shows the protective effect of the sizing. For lower laser powers, the sizing layer remains on the surface and fibers are not exposed (Fig. 5d).

We investigated the modifications in the chemical composition of the samples by electron-dispersive X-ray (EDX, Bruker, Quantax 200) analysis. The main change in chemical status is the change

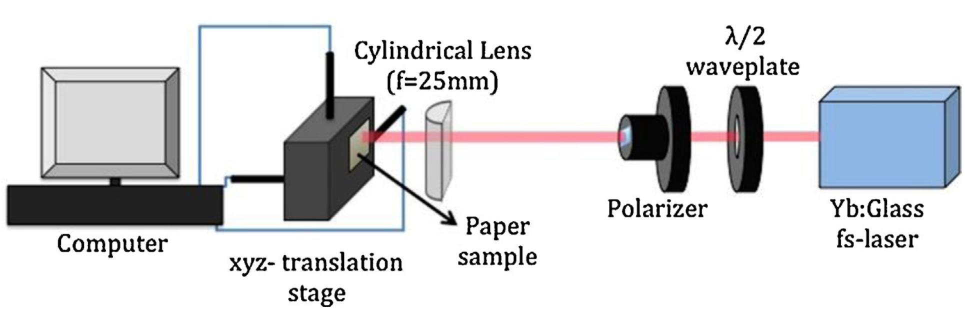

Fig. 1. Layout of the experimental setup for fs laser cleaning of paper.

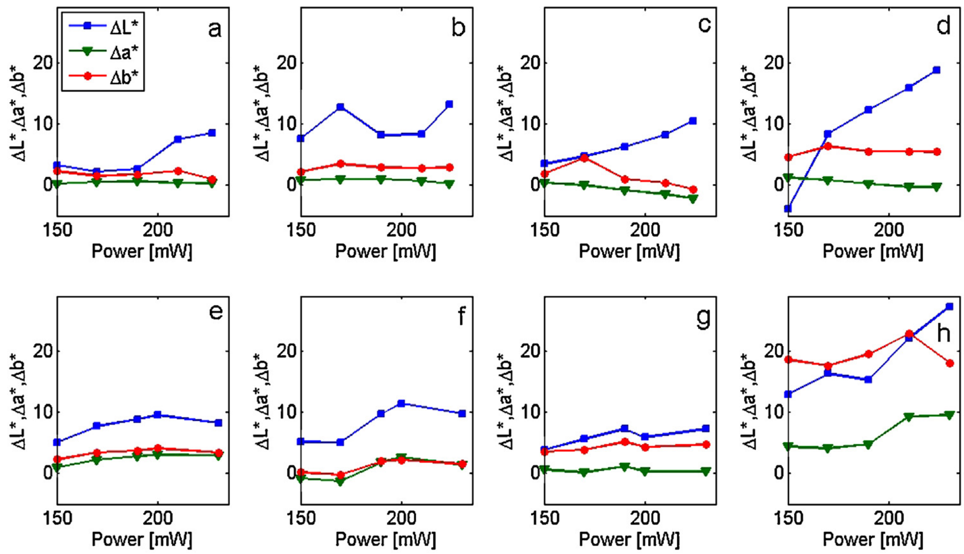

Fig. 2. Color measurements on various types of artificially contaminated papers cleaned at different laser powers. The top row corresponds to carbonaceous contaminants (graphite powder and glue) and the bottom row blue crayon marks. The samples are (from left to right) A1, A2, A3 and A4.

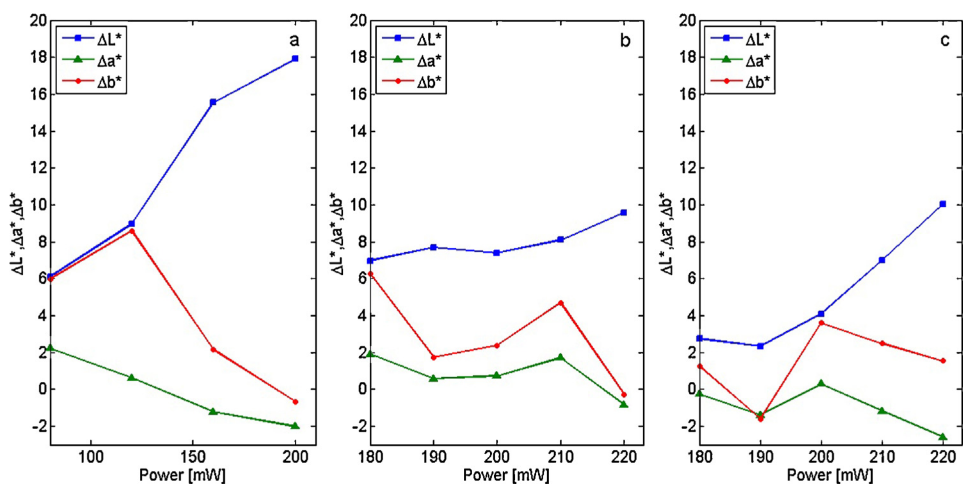

Fig. 3. Color measurements on the historical papers B1 (a), B2 (b) and B3 (c) cleaned at various laser powers.

of various oxides (such as SiO_2, SO_3, K_2O, CaO, FeO, Na_2O, MgO, Al_2O_3). The amounts of maximum change in oxidation of cleaned samples occur for SiO_2, and its increase at different laser powers are shown in Table 2. The most abundant elements detected, i.e. Al, Fe, K, Ca, Mg and Si, are normally not found in cellulose fibers and they are mainly present in the superficial layers (such as dust). On the other hand, the source of Al and K may be alum (potassium aluminum sulfate) which had been a widely used additive in paper manufacture. Moreover, Ca may also be originated from the presence of $CaCO_3$ that could had been used as a filler, or from lime [$Ca(OH)_2$], the use of which is well known in paper production.

4.3. Mechanical strength

After cleaning treatments, paper can become more brittle. To investigate the effect of laser cleaning on the mechanical strengths of the paper, we performed tensile stress tests on artificially soiled and aged samples. The samples were cut in dog-bone shape and then positioned on the materials testing machine (Llyod-LF plus). One end of the paper was fixed and the other was pulled with a constant speed of 3 mm/s. We recorded tensile strength at the time the paper broke. Mechanical strength results of treated papers are given in Fig. 6. For comparison, we also measured tensile strengths of untreated papers, and plot them as red-dashed reference lines in the corresponding figures.

The tensile tests show that in all cases of laser cleaning, weakening of the paper is unavoidable. Because of the non-uniform nature of the paper samples, we observe fluctuations in the tensile strengths. However, we also observe an overall trend of decrease of strengths with increasing laser power for the majority of the cases.

5. Discussions

In this section, we further discuss the experimental results we obtained. Firstly, we consider color changes after laser cleaning. Experimental results for artificially aged (Fig. 2) and historical

Table 2
Summary of laser cleaning results on historical papers.

Paper	Laser Power (mW)	ΔL^*	Δa^*	Δb^*	Max change in oxidation (%)	Fibers
B1	80	6.12	2.24	5.99	0.51	Unexposed
	200	17.91	−2.00	−0.65	9.43	Exposed
B3	180	2.75	−0.25	1.26	0.57	Unexposed
	220	10.04	−2.58	1.54	4.41	Unexposed

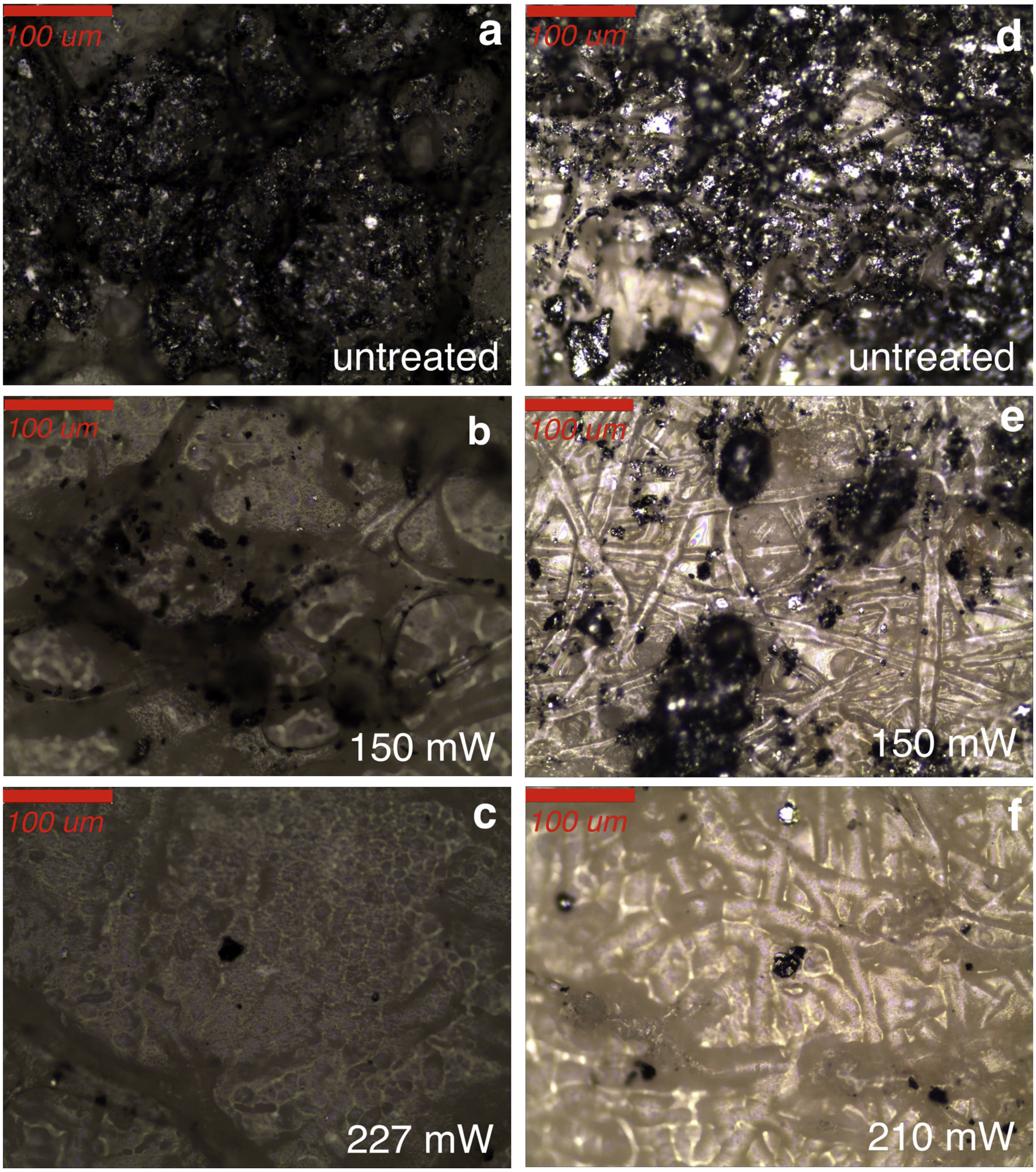

Fig. 4. Optical microscopy images of untreated and laser cleaned papers A1 (a-c) and A4 (d-f). The laser powers are indicated.

(Fig. 3) samples show that laser cleaning increases brightness in all cases, as expected from removal of darker-colored contaminants. Small deviations can be attributed to inhomogeneity of paper surfaces, especially of historical ones. Higher laser powers result in bleaching of the sample and can be avoided at low powers. As a result, a compromise between effectiveness of dirt removal and over-bleaching can be achieved by leaving small amounts of contaminants (often unnoticeable to naked eye) on surface. An example of cleaning with these considerations is shown in Fig. 7b.

Δa^* and Δb^* values are also of concern as they signal discoloration. In general, color changes greater than two units are perceivable by the human eye. For all carbonaceous soiled papers (Fig. 2, top row), reddening (Δa^*) and yellowing (Δb^*) are very close to or under the limit of perception. In the case of blue crayon stains (Fig. 2, bottom row), yellowing is mostly dominant, again as expected from the colored nature of the contaminant. For the historical samples, same general behavior is observed, while slightly higher color changes are observed in some cases (Fig. 3).

Another requirement for proper paper conservation is that the mechanical strength should not decrease significantly after cleaning. As papers comprise of cellulosic fibers, they are chemically and physically fragile. For this reason, cleaning treatment should not damage the fiber structure which determines the strength of paper. If fiber rows are broken and/or chemically impaired by means of laser irradiation, paper becomes more brittle and its strength diminishes. Therefore, it is a necessity to investigate strength of treated and untreated sample papers in order to understand the effect of laser cleaning on paper strength. From tensile experiments (Fig. 6), we observed that mechanical strengths of laser cleaned papers decrease as compared to untreated ones. This is an inevitable result due to the partial removal of surface layers (sizing or contaminants), that imparts strength to paper. If microstructure of the paper is not destroyed, the amount of change in strength can be deemed acceptable. In addition, as can be seen from Fig. 6, especially for lower laser powers, the change in the mechanical strength tends to be minimal. Comparison of samples with sizing (A1 and A4)

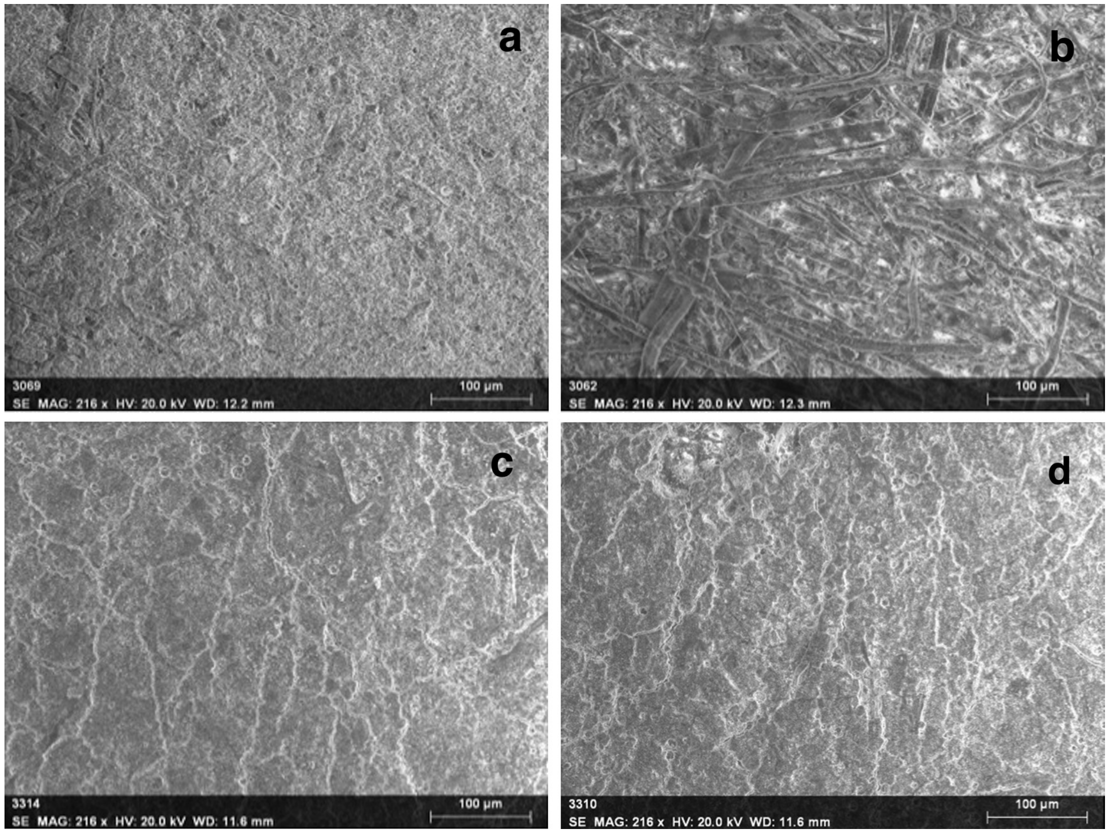

Fig. 5. SEM images of historical paper B1. Left column shows untreated and right column shows laser cleaned sections with average powers 200 mW (b) and 80 mW (d).

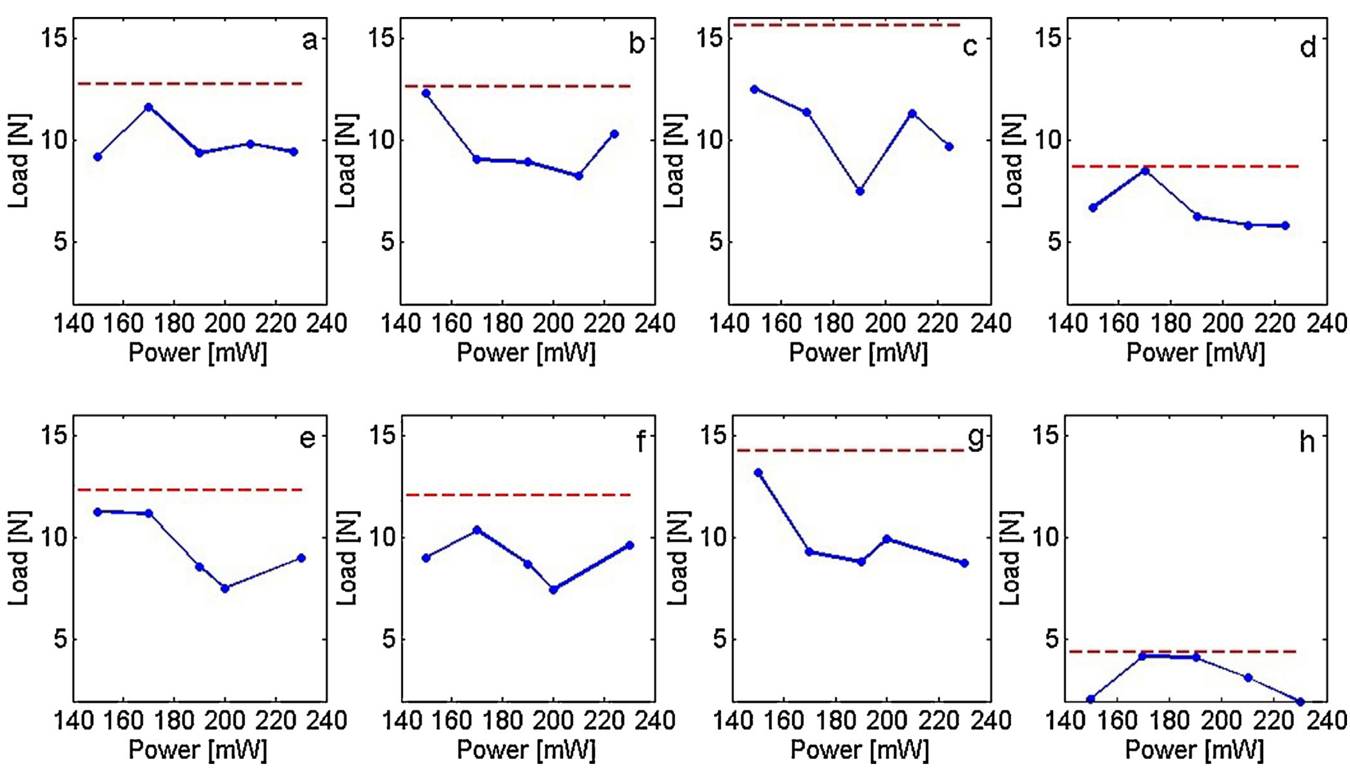

Fig. 6. Mechanical strength measurements on the papers cleaned at different laser powers. The top row corresponds to carbonaceous contaminants and the bottom row blue crayon marks. The samples are (from left to right) artificially aged A1, A2, A3 and A4.

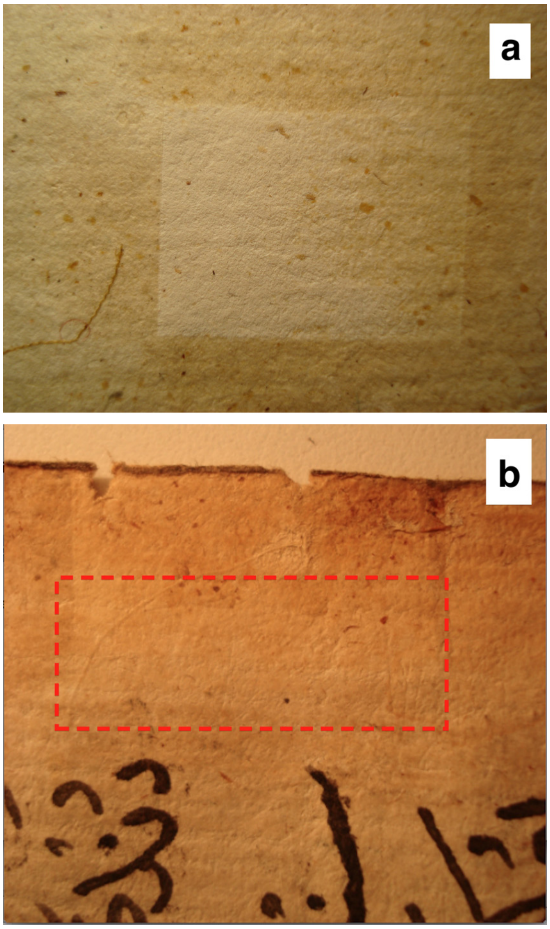

Fig. 7. Photos of historical papers cleaned with fs-laser, illustrating over-bleaching (a) and removal of glue stains with no discoloration (b). In (a) the rectangular, lighter colored region in the center is laser treated. In (b), cleaned area is indicated with overlaid rectangular dotted lines.

and without sizing (A2 and A3) shows that the latter exhibit higher maximum strength drop with respect to reference.

SEM analysis of historical papers enabled deeper examination on strength of papers and the status of fibers. SEM images confirm that, in all laser power regimes, fiber structures were intact (Fig. 5). Only for high laser powers, the cellulose fibers become exposed by excessive removal of sizing. For lower powers, laser cleaning is totally confined to the sizing level and fibers are not exposed at all. Therefore, one can say that fs-laser irradiation did not give rise to irreversible destructive effects on fibers because the sizing acted as a protective layer during the laser cleaning process.

Finally, visual and aesthetic results of any conservation process are of crucial importance. Even if contaminated regions are not over-bleached after laser cleaning, their appearance should be indistinguishable from originally clean regions and should not diminish the authenticity of the artifact. Close-up photographs of two different examples of cleaned historical papers are shown in Fig. 7. Fig. 7a shows a region of a blank paper, partially treated (rectangular region in the middle) by deliberately high laser power. In this case, the bleaching is excessive, as can be seen from comparison to untreated regions. On the other hand, in Fig. 7b, we show results on a historical paper, with excessive glue contaminants on the edges. It can be observed that the laser cleaning efficiently removes the glue from the edges; and after the cleaning, the appearance of the paper is visually indistinguishable with originally clean and untreated regions (the red-dotted rectangle in Fig. 7b contains the two regions). This result shows that when appropriate parameters are used, fs laser cleaning successfully removes stains from the surface of paper with sizing, and does not compromise the authentic appearance of the artifact.

6. Conclusions

In conclusion, we show that fs laser ablation can be a very effective way for cleaning of historical paper documents, particularly those with sizing. The incident laser fluence determines both the effectiveness of cleaning, as well as post-process status of the sample. Our investigations on effects of laser average power on colorimetric, microscopic and mechanical properties of the samples reveal that keeping the laser power close to the “cleaning threshold” is a safe way to prevent unwanted or excessive effects. In Table 2, we present a summary of results obtained on historical samples B1 and B3. It can be seen that modifications on the samples are minimal especially for low powers. In the case of B1, yellowing after treatment is higher for low powers, due to the original color of this particular paper. Our results demonstrate that the high precision and minimal side effect nature of fs laser ablation can be of significant interest in cleaning and conservation of historical paper documents. For future studies, further investigation of the effects of fs laser on the exposed fibers are to be performed. In addition, comparative studies of the effects of fs and nanosecond lasers, as well as those of different wavelengths (IR, visible and UV) can provide further details and possibilities on the proposed method.

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