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Cleaning of artificially soiled paper using nanosecond, picosecond and femtosecond laser pulses

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Abstract Cleaning of cultural assets, especially fragile organic materials like paper, is a part of the conservation process. Laser radiation as a non-contact tool offers prospects for that purpose. For the studies presented here, paper model samples were prepared using three different paper types (pure cellulose, rag paper, and wood-pulp paper). Pure cellulose serves as reference material. Rag and wood-pulp paper represent essential characteristics of the basic materials of real-world artworks. The papers were mechanically soiled employing pulverized charcoal. Pure and artificially soiled paper samples were treated with laser pulses of 28 fs (800 nm wavelength) and 8–12 ns (532 nm) duration in a multi pulse approach. Additionally, the cellulose reference material was processed with 30 ps (532 nm) laser pulses. Damage and cleaning thresholds of pure and soiled paper were determined for the different laser regimes. Laser working ranges allowing for removal of contamination and avoiding permanent modification to the substrate were found. The specimens prior and after laser illumination were characterized by light-optical microscopy (OM) and scanning electron microscopy (SEM) as well as multi spectral imaging analysis. The work extends previous nanosecond laser cleaning investigations on paper into the ultra-short pulse duration domain.

1 Introduction

Starting with the pioneering activities of John Frederic Asmus and coworkers more than 30 years ago [1], laser radiation has been used for cleaning of works of art. Laser cleaning can be considered as a well-established technique in stone conservation, while laser treatment of complex organic materials like paper, parchment, and textiles is still not fully developed for application in conservation workshops.

The main role of paper is that of a medium for conveying text and image. As soiling interferes with the perception of information, paper cleaning is needed. For a successful cleaning of paper, a laser working range has to be found allowing for removal of contamination without any deterioration of the paper matrix material.

During the last decade, various nanosecond pulse lasers were used in laboratories to clean paper. Cleaning of paper caused by ultraviolet excimer laser radiation [2–7] is accompanied by its unwanted potential to induce direct photolysis or photo-oxidative degradation of the fiber substrate material [7]. Avoiding high single photon energies, fundamental wavelength (1064 nm) and second harmonic (532 nm) of Nd:YAG lasers were applied for cleaning purposes [8–18]. Besides noticeable cleaning effects, color changes (yellowing) of the cellulose substrate as a result of thermal degradation of soiling materials were reported for 1064-nm-treatment [11] and even for 532-nm-processing [16]. Nevertheless, multi wavelength studies (1064 nm, 532 nm, 355 nm, 266 nm, 248 nm) in the nanosecond pulse duration range concluded that the most promising cleaning results were obtained for 532 nm laser radiation [13–15, 17]. Recently, results of 8-ns laser (532 nm) cleaning of artificially soiled Whatman filter paper were compared with conventional eraser cleaning. Satisfying laser cleaning effects without visible mechanical damage and yellowing of the paper were reached. Additionally, the laser cleaning efficacy was superior to that obtained by eraser cleaning [18].

The use of picosecond and femtosecond laser pulses for structuring of materials offers essential advantages com-

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pared to longer (nanosecond) pulses of the same wavelength. Material removal is localized and requires less energy than in the long-pulse domain. The heat influence onto the laser-generated structures is minimized resulting in negligible collateral damage. Pioneering femtosecond laser damage studies were performed on organic materials (polymers) [19, 20]. Up to now, only a few papers were concerned with femtosecond laser cleaning of works of art with the main focus on paintings [21–28].

In this paper, laser cleaning experiments on artificially soiled paper model samples are extended from the nanosecond (~10 ns, 532 nm) to the picosecond (30 ps, 532 nm) and femtosecond (28 fs, 800 nm) pulse duration range. For a multi pulse approach, laser-induced damage thresholds of paper substrates and cleaning thresholds were determined. The organic samples were inspected by optical and scanning electron microscopy. A safe laser working range for removal of contamination and avoiding of permanent modification to the substrate is evaluated. Safe means that no change of the fiber structure or yellowing of the paper matrix is observed.

2 Experimental

Three paper types were selected for the preparation of soiled model samples: Whatman filter paper No. 1, machined rag paper, and wood-pulp paper ("Aktstudienblock Nr. 34432", Vang). Whatman filter paper No. 1 consists of highly purified cellulose (no sizing) and serves as reference material. The fiber compositions of rag and wood-pulp paper are representative for papers existent in cultural collections. All papers were mechanically soiled with pulverized charcoal in a standardized procedure [18] to make model samples. Soiling particles up to 20 µm in size produced by mechanical abrasion of charcoal were brushed on the paper. The soiling dust was vacuum sucked into the paper. Afterwards an adherence between artificial pollution and paper was achieved by simultaneous action of brushing and vacuum treatment.

The homogeneity of the soiling was measured by means of a multi spectral imaging system (MUSIS 2007, Art Innovation). Lightness differences of $<10\%$ were found on the soiled samples in the visible spectral region (visible reflection mode of MUSIS). Additionally, MUSIS was used to analyze the cleaning status of the model samples after laser treatment. CIE $L^*a^*b^*$ (CIELAB) color coordinates were utilized. The CIELAB model features the parameters lightness of the color (L^*) and two chromaticity coordinates (a^*, b^*). Ideally, $L^* = 0$ yields black and $L^* = 100$ indicates white [18, 29]. In our case, a decreasing lightness difference (between reference and sample) ΔL^* can be correlated with a higher cleaning quality (reference white Whatman filter paper No. 1 as received: $\Delta L^* = 0$). In addition to the MUSIS investigations, samples were analyzed with optical (Eclipse L200, Nikon) and scanning electron microscopy (Stereoscan 180, Cambridge, accelerating voltage 10 kV).

Three lasers were employed for cleaning purposes covering a pulse duration range of more than five orders of magnitude. A Ti:sapphire laser (Femtopower Compact Pro, Femtolasers) emitted pulses with a duration of 28 fs at a central wavelength of 800 nm and at 1 kHz repetition rate. Two different Nd:YAG lasers (502-D.PS 7910, BMI and DINY pQ, IB Laser) delivered 532-nm laser pulses with 30 ps (10 Hz) and 8–12 ns (500 Hz) pulse duration. The pulses were focused on the paper surfaces to Gaussian beam radii ($1/e^2$) of 140 µm (fs), 90 µm (ps), and 40–100 µm (ns), respectively. Pulse energies were measured with two energy meters (3Sigma, Coherent and Nova, Ophir).

For femtosecond and picosecond laser operation, paper samples were mounted on motorized x–y-translation stages (LOT) to achieve cleaning of predefined areas. In the nanosecond case, the laser beam was scanned over the sample surface. For all pulse duration regimes, 100 pulses per spot (100-on-1) were selected. These particular illumination conditions were chosen as a worst-case scenario resulting in comparatively low damage thresholds of the paper matrices as a result of an incubation behavior.

3 Results and discussion

3.1 Laser interaction with pure paper substrates

Laser pulses were impinged on pure paper materials to determine damage thresholds. Figure 1 depicts scanning electron microscope pictures of the original surface and the surface of Whatman filter paper No. 1 after laser illumination close to the damage threshold. In Fig. 1a, the surface morphology of pure paper in its initial state can be seen. The cellulose fibers as basic material of the filter paper are illustrated. Figures 1b, c display an overview (Fig. 1b) and a detail (Fig. 1c) of a damage spot generated with femtosecond laser pulses at the damage threshold of the filter paper. A comparatively smooth cut in the complex material was obtained (Fig. 1c). An increase of the energy density of the ps laser by a factor of four in comparison to the fs case was necessary to reach the damage threshold (Fig. 1d) although the ps laser wavelength was shorter (800 nm vs. 532 nm). The damage spot in the center of the SEM picture is clearly visible. Figure 1e shows damaged cellulose fibers for nanosecond pulse laser processing. For 12-ns pulses at 532 nm wavelength, the paper withstands laser fluences of up to 10 J/cm^2. I.e., the nanosecond multi pulse damage threshold of pure Whatman filter paper is by more than an order of magnitude higher than the picosecond damage threshold.

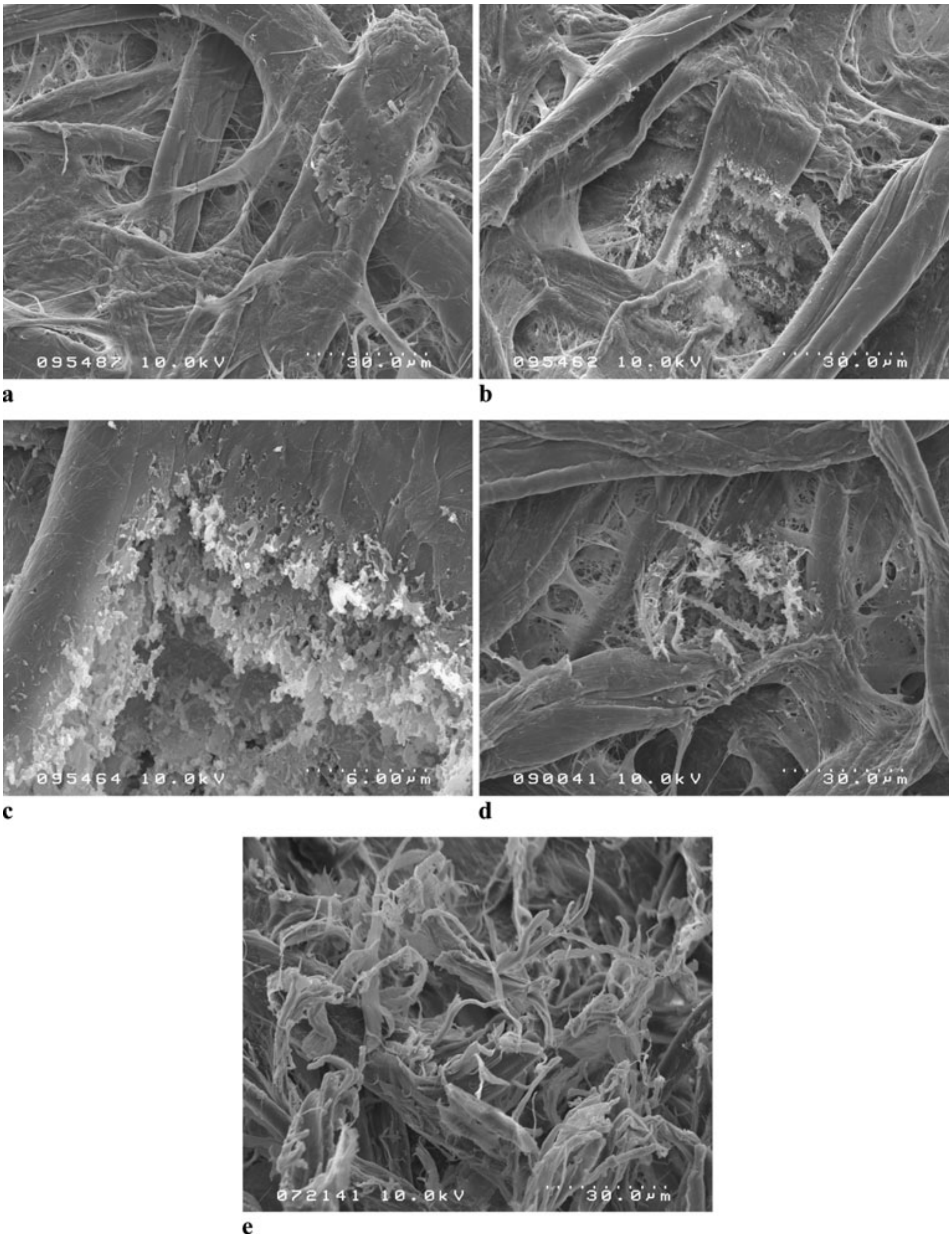


Fig. 1 SEM pictures of the surface of Whatman filter paper No. 1. As received (**a**). After pulse laser treatment (100-on-1) with (**b**, **c**) 28 fs, 0.19 J/cm^2, (**d**) 30 ps, 0.75 J/cm^2, (**e**) 12 ns, 10.1 J/cm^2

Figure 2 summarizes damage thresholds F_{th} of pure paper materials and an artificial soiling (charcoal dust on Whatman filter paper No. 1) for femtosecond, picosecond, and nanosecond laser impact. F_{th} for nanosecond laser illumination are by a factor of about 50 (Whatman filter paper), 13 (rag paper), and 6 (wood-pulp paper) higher than F_{th} for the femtosecond laser. In the fs case, F_{th} value shows only a slight variance between the paper types while a significant change of F_{th} is found for the application of ns pulses. A nonlinear absorption of laser radiation is much more probable for fs than for ns radiation. Therefore, F_{th} becomes independent of the structure of the (linearly non-absorbing) paper materials for fs laser illumination. For ns laser impingement, F_{th} of Whatman filter paper which can be considered as highly purified cellulose with no sizing is considerably higher than those of rag and wood-pulp paper. The latter ones may contain additives (binder, filler) in addition to the fiber matrix resulting in higher remnant absorption and therefore lower damage thresholds.

3.2 Laser cleaning of artificially soiled model samples

Cleaning thresholds are of the order of a few 10 mJ/cm^2 for all pulse duration regimes (Fig. 2). Multi pulse cleaning thresholds of the dust films were detected by naked eye and microscopically from series of experiments with varying laser fluence. For the different laser types, F_{th} were determined using single laser spots (fs and ps) and laser-produced squares with 3 mm edge length (ns), respectively. In literature, single pulse damage thresholds (100–120 fs, 780–800 nm) of the order of 100 mJ/cm^2 of bulk graphite were reported [30, 31]. Additionally, damage thresholds of thin absorbing films can be reduced with decreasing layer thickness in the nanosecond [32] and even in the femtosecond pulse duration range [33] explaining qualitatively lower F_{th} of the soiling compared to bulk graphite values.

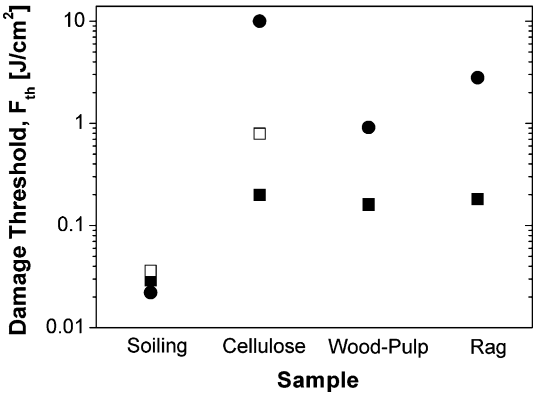
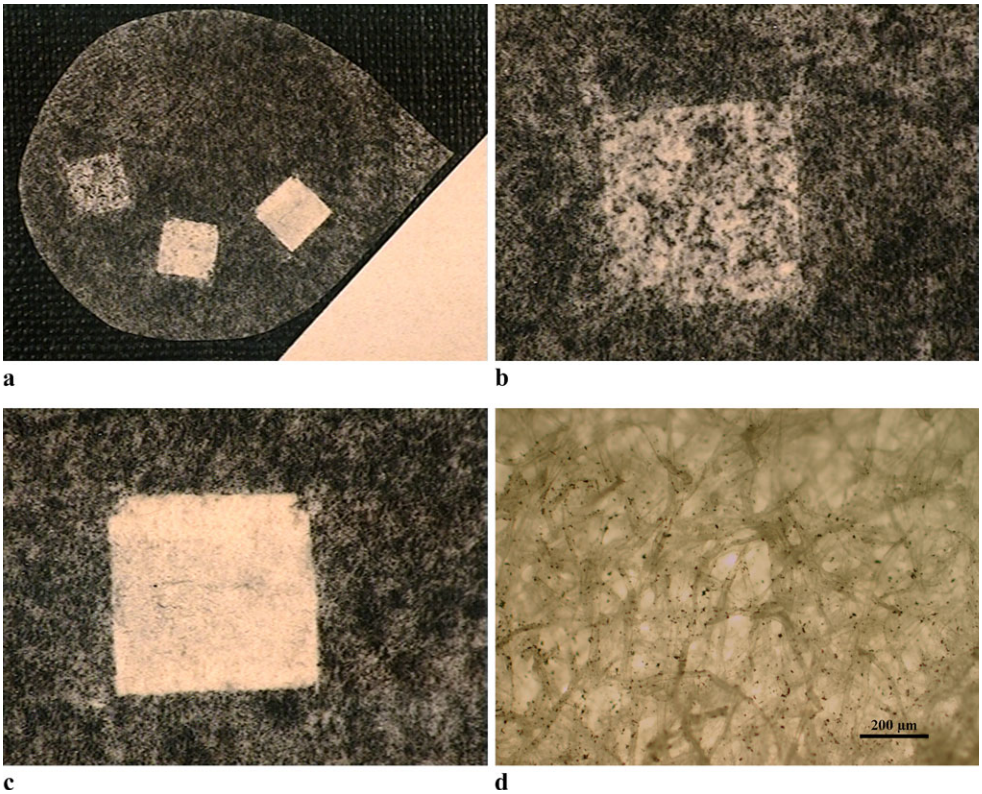


Fig. 2 Damage thresholds F_{th} for multi pulse (100-on-1) laser treatment of artificial soiling, pure cellulose, wood-pulp paper, and rag paper employing pulse durations of 28 fs (■), 30 ps (□), and 12 ns (●), respectively

Figures 3 and 4 show cleaned squares each with an edge length of 5 mm on artificially soiled Whatman filter paper employing femtosecond (Fig. 3) and nanosecond (Fig. 4) laser pulses. For both pulse durations, laser energy densities of 0.05 J/cm^2, 0.10 J/cm^2, and 0.15 J/cm^2, i.e. above cleaning and below damage threshold of the paper, were applied. A MUSIS overview picture of the cleaned areas (Figs. 3a, 4a) and a higher magnification of the cleaning results for 0.05 J/cm^2 (Figs. 3b, 4b) and 0.15 J/cm^2 (Figs. 3c, 4c) are depicted. The central parts of the cleaned areas of Figs. 3c and 4c were inspected by means of OM (Figs. 3d, 4d). For equal laser fluence, a comparison of the pictures of the cleaning results suggests a higher cleaning efficiency for the fs laser application in comparison to the ns case. Especially the OM micrographs demonstrate a better cleaning success in the fs case. This finding is supported by MUSIS lightness difference measurements in the visible reflection mode (Table 1). ΔL^* for laser processing with 0.15 J/cm^2 is considerably lower in the fs compared to the ns case ($\Delta L^*_{\mathrm{fs}} = 5$ vs. $\Delta L^*_{\mathrm{ns}} = 24$).

Soiled Whatman filter paper was cleaned with laser fluences amounting 50% of the multi pulse damage threshold value of pure paper for fs ($F_{\mathrm{th}} = 0.2$ J/cm^2) and ns ($F_{\mathrm{th}} = 10$ J/cm^2) pulses. Central parts of cleaned areas of 5 mm × 5 mm are displayed in Fig. 5. Obviously, cleaning efficacy of ns laser treatment with a laser fluence of 5.0 J/cm^2 (Fig. 5b) was superior to that obtained with 0.1 J/cm^2 and fs laser illumination (Fig. 5a). MUSIS lightness difference

Fig. 3 MUSIS pictures (**a**–**c**) and OM micrograph (**d**) of Whatman filter paper artificially soiled with charcoal after femtosecond laser cleaning (28 fs). Each square with an edge length of 5 mm was processed with 100 pulses per spot. (**a**) Overview of three cleaned areas. Laser fluences of 0.05 J/cm^2 (*left*), 0.10 J/cm^2 (*middle*), and 0.15 J/cm^2 (*right*) were used. Lower right corner: Whatman filter paper without soiling as reference. (**b**) Cleaned square (0.05 J/cm^2). (**c**) Cleaned square (0.15 J/cm^2). (**d**) Central section after fs laser processing (0.15 J/cm^2)



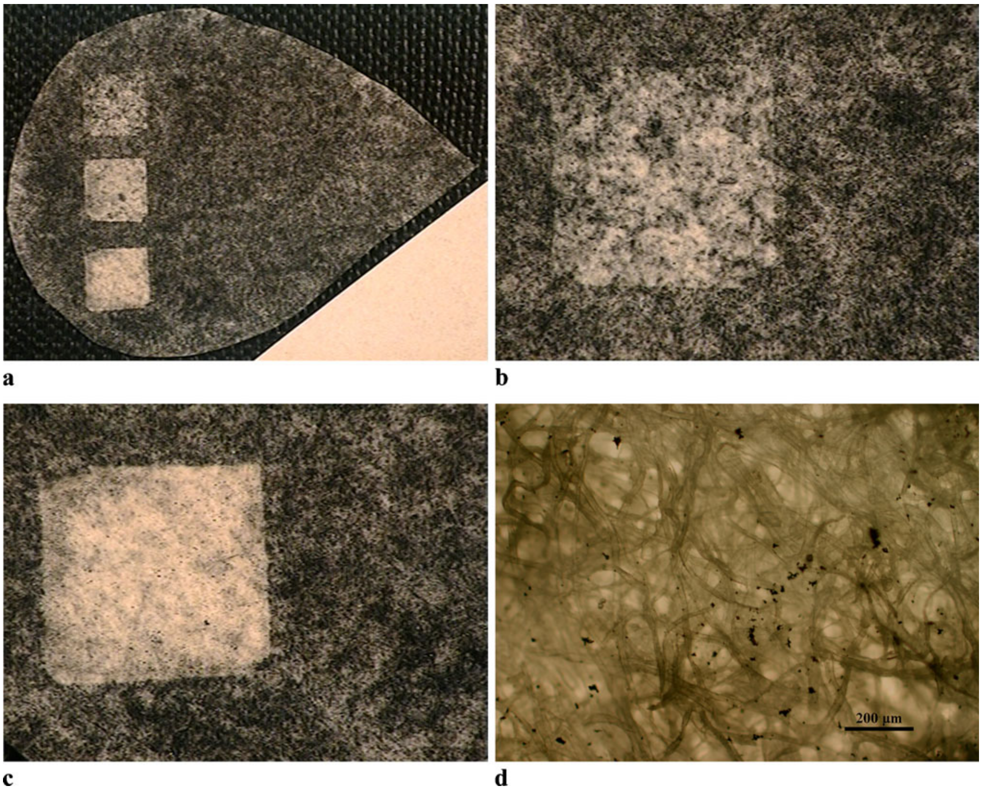


Fig. 4 MUSIS pictures (**a**–**c**) and OM micrograph (**d**) of Whatman filter paper artificially soiled with charcoal after nanosecond laser cleaning (8 ns). Each square with an edge length of 5 mm was processed with 100 pulses per spot. (**a**) Overview of three cleaned areas. Laser fluences of 0.05 J/cm^2 (at the *top*), 0.10 J/cm^2 (*middle*), and 0.15 J/cm^2 (*bottom*) were used. Lower right corner: Whatman filter paper without soiling as reference. (**b**) Cleaned square (0.05 J/cm^2). (**c**) Cleaned square (0.15 J/cm^2). (**d**) Central section after ns laser processing (0.15 J/cm^2)

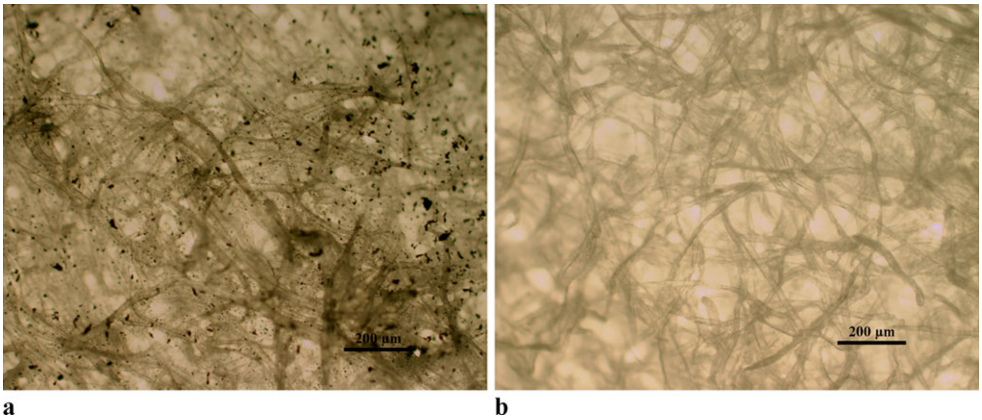


Fig. 5 OM pictures of femtosecond and nanosecond laser cleaned areas of artificially soiled Whatman filter paper at laser fluences of 50% of the damage threshold value of pure paper. (**a**) 28 fs, 0.10 J/cm^2, (**b**) 8 ns, 5.0 J/cm^2

Table 1 Multi pulse laser cleaning of artificially soiled Whatman filter paper No. 1. Lightness difference ΔL^* in dependence on laser fluence for the application of femtosecond and nanosecond pulses. Reference value for the soiled sample: $\Delta L^* = 73$

Laser fluence (J/cm^2)	ΔL^*_{fs}	ΔL^*_{ns}
0.05	39	41
0.10	9	36
0.15	5	24
1.0		3
2.0		2
5.0		0

measurements yielded $\Delta L^*_{\mathrm{fs}} = 9$ and $\Delta L^*_{\mathrm{ns}} = 0$. The latter value means that the level of a clean reference sample was reached. Nearly equal cleaning thresholds of charcoal dust for fs (800 nm), ps (532 nm), and ns (532 nm) laser treatment and higher substrate damage thresholds in the long-pulse case lead to a larger working range for ns laser pulses (compare Fig. 2). Application of higher laser fluences can result in an equal (or even better) cleaning quality compared to the ultra-short pulses. Using the same laser fluence in both cases, cleaning efficiency of femtosecond laser radiation is higher compared to the nanosecond case.

It should be noted that hidden chemical changes or modifications of the mechanical strength of the papers as a result of laser impact were beyond the scope of this paper. Nevertheless, yellowing of the papers was not found.

4 Conclusions

Laser cleaning investigations on artificially soiled paper model samples were presented using nanosecond ($\sim$10 ns, 532 nm), picosecond (30 ps, 532 nm), and femtosecond (28 fs, 800 nm) pulses. Multi pulse (100-on-1) damage thresholds of pure paper substrates were higher for long pulses regardless of the paper type. Cellulose as reference material withstood laser fluences of about 10 J/cm^2 for ns pulses, 0.8 J/cm^2 for ps pulses while energy densities of 0.2 J/cm^2 led to damage of the material in the fs case. Laser cleaning thresholds (removal of the soiling) of a few 10 mJ/cm^2 were observed for all pulse durations. For cellulose, wood-pulp paper, and rag paper, larger working ranges were found for the nanosecond domain compared to the femtosecond regime. For the same laser fluence (within the laser working range), cleaning efficiency was higher for femtosecond laser radiation compared to nanosecond pulse illumination. With ns laser pulses, an equal (or even better) cleaning quality was achieved when high laser fluences (below substrate damage threshold) were applied.

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References

1. L. Lazzarin, L. Marchesi, J.F. Asmus, J. Vac. Sci. Technol. **10**, 1039 (1973)
2. T.R. Friberg, V. Zafiropulos, M. Kalaitzaki, R. Kowalski, J. Petrakis, C. Fotakis, Lasers Med. Sci. **12**, 55 (1997)
3. W. Kautek, S. Pentzien, P. Rudolph, J. Krüger, E. König, Appl. Surf. Sci. **127–129**, 746 (1998)
4. J.P. Duarte, P. Pecas, Rev. Metall. **34**, 101 (1998)
5. O.D.D. Soares, R.M. Miranda, J.L.C. Costa, Appl. Opt. **38**, 6307 (1999)
6. E. Sarantopoulou, Z. Samardzija, S. Kobe, Z. Kollia, A.C. Cefalas, Appl. Surf. Sci. **208**, 311 (2003)
7. J. Kolar, M. Strlič, S. Pentzien, W. Kautek, Appl. Phys. A **71**, 87 (2000)
8. J.M. Lee, K.G. Watkins, Opt. Las. Eng. **34**, 429 (2000)
9. J.M. Lee, W.M. Steen, Int. J. Adv. Manuf. Technol. **17**, 281 (2001)
10. J. Kolar, M. Strlič, M. Marinček, Appl. Phys. A **75**, 673 (2002)
11. M. Strlič, J. Kolar, V.S. Ŝelih, M. Marinček, Appl. Surf. Sci. **207**, 236 (2003)
12. K. Ochocinska, M. Sawczak, M. Martin, J. Bredal-Jorgensen, A. Kaminska, G. Sliwinski, Rad. Phys. Chem. **68**, 227 (2003)
13. P. Rudolph, F.J. Ligterink, J.L. Pedersoli Jr., M. van Bommel, J. Bos, H.A. Aziz, J.B.G.A. Havermans, H. Scholten, D. Schipper, W. Kautek, Appl. Phys. A **79**, 181 (2004)
14. P. Rudolph, F.J. Ligterink, J.L. Pedersoli Jr., H. Scholten, D. Schipper, J.B.G.A. Havermans, H.A. Aziz, V. Quillet, M. Kraan, B. van Beek, S. Corr, H.-Y. Hua-Ströfer, J. Stokmans, P. van Dalen, W. Kautek, Appl. Phys. A **79**, 941 (2004)
15. A. Kaminska, M. Sawczak, M. Cieplinski, G. Sliwinski, B. Kosmowski, Opt. Appl. **34**, 121 (2004)
16. M. Strlič, V.S. Ŝelih, J. Kolar, D. Kočar, B. Pihlar, R. Ostrowski, J. Marczak, M. Strzelec, M. Marinček, L.S. Johansson, Appl. Phys. A **81**, 943 (2005)
17. A. Kaminska, M. Sawczak, K. Komar, G. Sliwinski, Appl. Surf. Sci. **253**, 7860 (2007)
18. J. Krüger, S. Pentzien, A. Conradi, Appl. Phys. A **92**, 179 (2008)
19. S. Küper, M. Stuke, Appl. Phys. B **44**, 199 (1987)
20. R. Srinivasan, E. Sutcliffe, B. Braren, Appl. Phys. Lett. **51**, 1285 (1987)
21. J. Shepard, C.R.T. Young, D. Parsons-Karavassilis, K. Dowling, Opt. Life Sci. **5**, 108 (2000)
22. T. Burmester, M. Meier, H. Haferkamp, S. Barcikowski, J. Bunte, A. Ostendorf, in *Lasers in the Conservations of Artworks*, ed. by K. Dickmann, C. Fotakis, J.F. Asmus. Springer Proceedings in Physics, vol. 100 (Springer, Berlin, 2005) p. 61
23. P. Pouli, G. Bounos, S. Georgiou, C. Fotakis, in *Lasers in the Conservations of Artworks*, ed. by J. Nimmrichter, W. Kautek, M. Schreiner. Springer Proceedings in Physics, vol. 116 (Springer, Berlin, 2007) p. 287
24. A.V. Rode, K.G.H. Baldwin, A. Wain, N.R. Madsen, D. Freeman, P. Delaporte, B. Luther-Davies, Appl. Surf. Sci. **254**, 3137 (2008)
25. A.V. Rode, D. Freeman, K.G.H. Baldwin, A. Wain, O. Uteza, P. Delaporte, Appl. Phys. A **93**, 135 (2008)
26. M. Walczak, M. Oujja, L. Crespo-Arca, A. Garcia, C. Mendez, P. Moreno, C. Domingo, M. Castillejo, Appl. Surf. Sci. **255**, 3179 (2008)
27. S. Gaspard, M. Oujja, P. Moreno, C. Mendez, A. Garcia, C. Domingo, M. Castillejo, Appl. Surf. Sci. **255**, 2675 (2008)
28. P. Pouli, A. Nevin, A. Andreotti, P. Colombini, S. Georgiou, C. Fotakis, Appl. Surf. Sci. **255**, 4955 (2009)
29. DIN 6174:1979-01: *Colorimetric evaluation of colour differences of surface colours according to the CIELAB formula* (1979)
30. S. Amoruso, G. Ausanio, M. Vitiello, X. Wang, Appl. Phys. A **81**, 981 (2005)
31. M. Lenner, A. Kaplan, C. Huchon, R.E. Palmer, Phys. Rev. B **79**, 184105 (2009)
32. G. Daminelli, S. Pentzien, A. Hertwig, J. Krüger, Appl. Phys. A **83**, 89 (2006)
33. J. Krüger, D. Dufft, R. Koter, A. Hertwig, Appl. Surf. Sci. **253**, 7815 (2007)