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ORIGINAL

Leaching effect of water on photodegraded hardwood species monitored by IR spectroscopy

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Abstract

Black locust (*Robinia pseudoacacia* L.), beech (*Fagus sylvatica* L.), aspen (*Populus tremula* L.) and sessile oak (*Quercus petraea* Liebl.) hardwood samples were irradiated by a strong ultraviolet (UV) emitter mercury lamp at 50 °C. Other series of specimens were exposed to a combined treatment of UV irradiation and water leaching. Ratio of UV radiation and water leaching time was 2:1. While the total duration of UV radiation was 20 days for both test series that of water leaching was 10 days. IR measurement was taken after both UV radiation and water leaching to monitor both effects separately. Lignin degradation proved to be more intensive in leached samples than in purely UV-irradiated samples. Guaiacyl and syringyl lignin showed similar degradation properties. Unconjugated carbonyl groups generated by the photodegradation were the most sensitive chemical components to leaching. Photodegradation generated two absorption bands of unconjugated carbonyl groups at around 1710 and 1760 cm^{-1} wavenumbers. The band at 1760 cm^{-1} was much more sensitive to water leaching than the band at 1710 cm^{-1}. Three to ten days of water leaching was enough to remove all unconjugated carbonyls generated by the photodegradation, depending on the species. Sessile oak was the most sensitive species to water leaching, whereas black locust proved to be the most stable against both photodegradation and water leaching. Water was able to leach out unconjugated carbonyl groups (absorbing at 1745 cm^{-1}) originally present in all investigated wood species.

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Introduction

Wood is a renewable material bonding large amounts of carbon. Growing trees absorb carbon dioxide from the atmosphere and convert it to woody biomass (Bravo et al. 2017). Half of the total wood mass is bonded carbon absorbed from the atmosphere. From an environmental aspect, it is important to store this carbon in wood products as long as possible ensuring slower wood decomposition and a long-term carbon cycle (Sathre and Gustavsson 2009; Keith et al. 2015). Taking into account the forested area of our planet, a significant amount of carbon can be stored in wood material for decades or even centuries, depending on the application. Therefore, wood products can play a significant role in the fight against global warming induced by greenhouse gases. Whether trees naturally decompose or burn, carbon dioxide is emitted back into the atmosphere. Carbon storage may be prolonged applying wooden products with longer life cycle. It is, therefore, in our common interest to ensure the longest possible life cycle for our wooden applications (Geng et al. 2017).

Customers appreciate aesthetic wooden surfaces for their pleasant visual appearance. Appealing textural features as well as other favourable properties of this biomaterial confer big advantages to both its interior and exterior usage. Organic materials like wood, however, undergoe biotic and abiotic degradation. The duty of sciences is to reduce these degradation effects without damaging the environment. For this purpose, detailed description of these degradation processes must be revealed.

The two most destructive abiotic phenomena for outdoor wooden applications are UV radiation of the sun and the leaching effect of the rain. Photodegradation of wood is a widely investigated phenomenon (Tolvaj and Faix 1995; Pandey 2005; Agresti et al 2013; Yildiz et al. 2013; Varga et al. 2017; Preklet et al. 2018; Broda and Popescu 2019; Liu et al. 2016, 2019a, b, c). Chemical analyses show that the surface degradation of wood is related primarily to the decomposition of lignin. The chromophoric groups of lignin are strong UV light absorbers, and the energy of UV photons absorbed is large enough to create free phenoxyl radicals. These free radicals react with oxygen to generate carbonyl groups (Colom et al. 2003; Pandey 2005; Teaca et al. 2013; Timar et al. 2016). Degradation products of lignin are responsible for yellowing of the surface (Calienno et al. 2015; Cogulet et al. 2016).

Most of the extractives are also sensitive to UV radiation. Black locust wood turns its yellow colour towards red within one-hour UV radiation. Extractives determine the natural colour of wood and the colour change is an excellent indicator for monitoring the alterations of extractive content (Chang et al. 2010; Fan et al. 2010).

The leaching effect of rain is the second most harmful effect during outdoor weathering of wood. The rain can leach out extractives (Kannar et al. 2018; Bejo et al. 2019) and consequently the colour of wood turns towards grey during long-term outdoor exposure (Tolvaj and Papp 1999). The effect of water leaching is a much less investigated phenomenon than the photodegradation. Some papers deal with simultaneous light exposure and water leaching during artificial weathering (Kamdem and Greiler 2002; Hansmann et al. 2006; Fufa et al. 2013). In these studies, the combined effect of photodegradation and water leaching was investigated, but individual impact of light exposure and water leaching was not separated. A preliminary research was published in a book (Csanady et al. 2015) presenting the leaching effect of water during the photodegradation of beech wood. The results showed that the unconjugated carbonyl groups were partly leached out by water. Another paper investigated separately the effects of UV irradiation and water leaching on spruce wood. Chemical changes were monitored by infrared (IR) spectroscopy. "As a consequence of photodegradation, two absorption bands of unconjugated carbonyl groups emerged at 1714 and 1750 cm^{-1} wavenumbers. The band at 1750 cm^{-1} was much more sensitive to leaching by water than the band at 1714 cm^{-1}. This band almost disappeared after eight cycles" (Bejo et al. 2019).

The aim of the present study was to investigate systematically the individual alteration effect of UV light exposure and water leaching separately during artificial weathering of hardwood species. A systematic treatment was designed consisting of UV radiation and water leaching in a 2:1 exposure ratio.

Materials and methods

For the present investigation, hardwood species with different extractive contents were chosen, namely black locust (*Robinia pseudoacacia* L.), beech (*Fagus sylvatica* L.), aspen (*Populus tremula* L.) and sessile oak (*Quercus petraea* Liebl.). While black locust and sessile oak timbers have high but diverse extractive content, beech timber is characterised by medium and aspen by low extractive content. The dimensions of specimens were 30 mm × 10 mm × 5 mm (long. × tang. × rad.). The heartwood of black locust and oak was used for the test. All investigated series were represented by 3 samples. IR measurement was taken on two fixed locations of the tangential surface of each sample. Tangential surface of the specimens contained only earlywood in case of black locust, aspen and oak. Sun radiation and leaching effect of the rain, as the main harmful factors affecting the degradation of outdoor wood, were simulated by the following experiments. Samples were irradiated by mercury lamp, then, plunged into distilled water at 22 °C (wet treatment). A double mercury vapour lamp with a total electric power of 800 W generated the light irradiation. The UV radiation was 80% of the total emission of the lamps. Specimens were located at a distance of 64 cm from the lamp. The temperature in the chamber was 50 °C during the irradiation. In the first cycle, UV radiation time was 24 h, followed by water leaching for 24 h, while in the second cycle, UV radiation time was doubled; 48-h UV radiation was followed by 24-h water leaching. The shorter UV radiation time was chosen at the beginning of the treatment because the degradation effect of UV radiation is very intensive at the beginning of the treatment. The treatments were repeated up to 20 days UV radiation and 10 days water leaching (Table 1). The other series of specimens were subjected to UV radiation only without water leaching (dry treatment). The initial weight of the samples was measured at the beginning of the treatments. Wet samples were dried at room temperature up to the initial weight to generate equal moisture content for all IR measurements.

Table 1 Order of UV irradiation and water leaching during the treatments

	UV irradiation (UV)	Water leaching (w)	Result
1. Cycle	1 day		1UV
		1 day	1UV + 1w
2. Cycle	2 days		3UV + 1w
		1 day	3UV + 2w
3. Cycle	2 days		5UV + 2w
		1 day	5UV + 3w
4. Cycle	2 days		7UV + 3w
		1 day	7UV + 4w
5. Cycle	2 days		9UV + 4w
		1 day	9UV + 5w
6. Cycle	2 days		11UV + 5w
		1 day	11UV + 6w
7. Cycle	2 days		13UV + 6w
		1 day	13UV + 7w
8. Cycle	2 days		15UV + 7w
		1 day	15UV + 8w
9. Cycle	2 days		17UV + 8w
		1 day	17UV + 9w
10. Cycle	3 days		20UV + 9w
		1 day	20UV + 10w

Diffuse reflectance infrared Fourier transform (DRIFT) spectrum of the samples was measured before and after treatments. Measurements were taken with an IR spectrophotometer (JASCO FT/IR 6300). The resolution was 4 cm^{-1}, and 64 scans were measured and averaged. The background spectrum was obtained against an aluminium plate. Two-point baseline correction at 3800 cm^{-1} and at 1900 cm^{-1} was carried out. The spectral intensities were calculated in Kubelka–Munk (K–M) units. The spectra were normalised to the band maximum around 1375 cm^{-1}. The intensity of spectra was adjusted to 1.0 by this normalisation at maximum around 1375 cm^{-1}. This C–H band of cellulose is often used as internal standard because of its high intensity, central position and strong stability. The difference spectrum was calculated by subtracting the initial IR data from the data of the treated sample. In this case, absorption increase is represented by positive band while negative band represents absorption decrease. Details of IR data manipulations and the band assignment are described in a previous work (Csanady et al. 2015).

Results and discussion

As already emphasised, the investigated species were chosen because of their diverse extractive content. Water-soluble extractives were in focus of our interest. Coldwater soluble extractive content of black locust ranges from 1.9 to 8.3%. Similar data for oak and beech are 3.6–5.7% and 1.9%, respectively (Wagenführ 2007). Aspen has data only for hot water soluble extractives (2.9%) in Wagenführ (2007). The main extractive components of black locust heartwood are the flavonoids. Flavonoids give 89% of the total extractive content. Within flavonoids, dihydrorobinetin is the main component covering 58% of total flavonoid content. The robinetin content covers 14% of total flavonoid content (Sanz et al. 2011). Sessile oak is less rich in extractives than most of the other oak species. The total extractive content of sessile oak was found to be 3.4% in a recent study (Baar et al. 2020).

The difference IR spectrum of wood gives information about the chemical changes generated by the applied treatment. The fingerprint area (900–1900 cm^{-1}) is presented in this work because the main differences were found in this region. The fingerprint region consists of the highly overlapping absorption bands of the main components of wood. The advantage of the difference spectrum method is that only the absorption changes are visible. Figure 1 represents the effect of 1-day UV irradiation on the investigated hardwood species. The main changes are similar for all investigated species. The absorption around 1509 cm^{-1} decreased representing the degradation of guaiacyl lignin (Colom et al. 2003; Csanady et al. 2015; Varga et al. 2017). The exact places of the minima are 1512, 1505, 1506 and 1512 cm^{-1} for black locust, beech, aspen and oak, respectively. This negative peak is visible together with the absorption decrease in the aromatic C–H deformation at around 1469 and 1428 cm^{-1} and with the absorption decrease in the guaiacyl ring breathing at around 1267 cm^{-1}. Comparing the species according to the degradation rate of guaiacyl lignin, black locust showed the smallest degradation followed by oak. The guaiacyl lignin in beech and aspen samples suffered greater degradation than in black locust and oak. This tendency remained during the whole 20-day irradiation.

Absorption decrease in syringyl lignin is visible at around 1597 cm^{-1} (Colom et al. 2003; Csanady et al. 2015; Varga et al. 2017). The exact places of the minima are at 1603, 1595, 1593 and 1597 cm^{-1} for black locust, beech, aspen and oak, respectively. The absorbed UV photons create free phenoxyl radicals by splitting the aromatic ring of lignin. These free radicals react with oxygen to generate

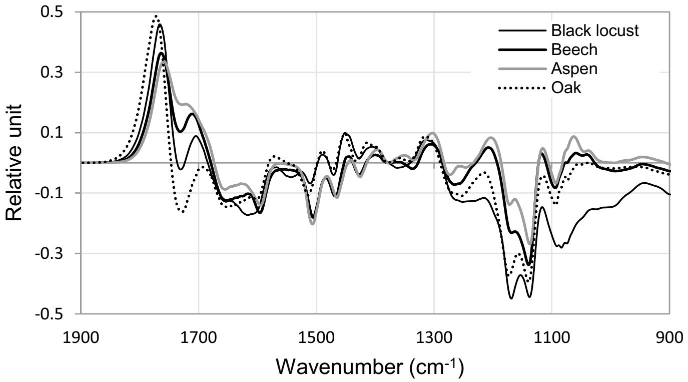

Fig. 1 Difference IR spectra of the investigated hardwood species generated by 1 day UV irradiation

carbonyl groups. As a consequence of lignin degradation, the intensity of unconjugated carbonyl band increased between 1680 and 1820 cm^{-1}. These bands represent the absorption of C=O stretching for aliphatic carboxyl groups, unconjugated ketones and gamma lactones. The unconjugated carbonyl region consists of two visible bands at around 1705 and 1765 cm^{-1} wavenumbers. (These two bands partly overlap each other generating the shift of the maxima towards each other during the treatments.)

Two absorption decreases are visible at around 1174 and 1137 cm^{-1}. The first decrease belongs to the asymmetric stretching of ether bond while the second one belongs to the symmetric stretching of ether bond, the aromatic C–H deformation and to the glucose ring vibration (Tolvaj and Faix 1995; Tolvaj et al. 2013). These absorption decreases indicate the ether splitting and the degradation of cellulose. There is a positive peak at 1066 cm^{-1} for beech and aspen. This positive peak is associated with the C–O and C–C stretching in cellulose and hemicelluloses. Popescu et al. (2013) found that the intensity increase in the band at 1058 cm^{-1} indicates the formation of aliphatic alcohols during thermal treatment at 140 °C.

There are differences among the investigated species according to the absorption intensity change around 1174 cm^{-1}. It is an intensive negative band for black locust and oak. In contrast, this band is visible as a shoulder for beech and aspen. The other differences among the investigated species are visible in the 1590–1720 cm^{-1} wavenumber interval. This is the absorption region of conjugated carbonyl groups, to be found mainly in the extractives. These groups are responsible for the colour of wood. The investigated species present similar moderate absorption decrease around 1645 cm^{-1}. The difference IR spectra of oak are shifted towards the negative values in the 1680–1720 cm^{-1} wavenumber interval. This negative shift disappeared after 3-day UV irradiation. The reason of this shift is unknown, but the extractives might be responsible for this phenomenon.

Figure 2 presents the effects of the first UV treatment and water leaching for beech samples. The thin solid line shows the chemical changes after 1-day UV

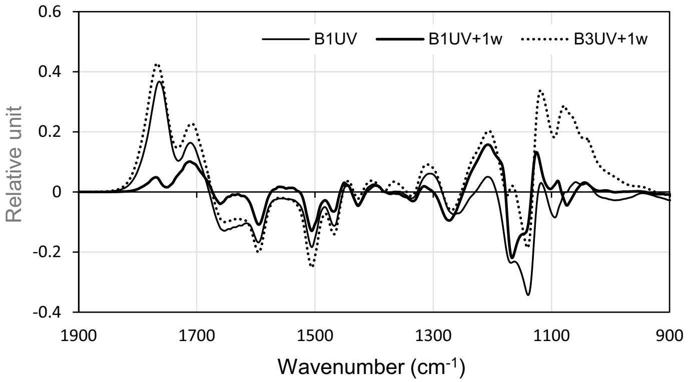

Fig. 2 Difference IR spectra of beech (B) generated by UV radiation and water leaching. Legends: 1UV = 1-day UV treatment, *x*UV + *y*w, where *x* is the duration of UV treatment and *y* is the duration of water leaching treatment in days

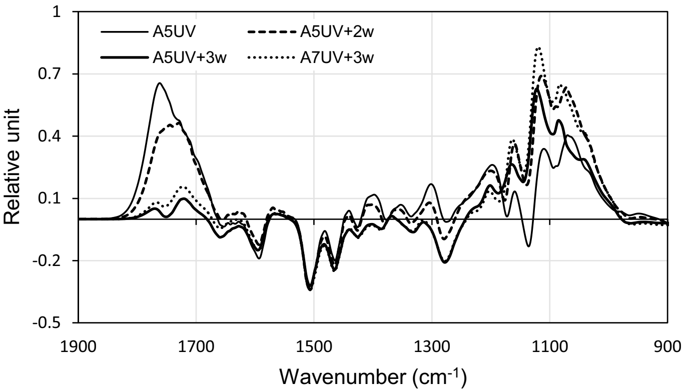

Fig. 3 Difference IR spectra of aspen (A) generated by UV radiation and water leaching. Legends: 5UV = 5-day UV treatment, ***x***UV + ***y***w, where ***x*** is the duration of UV treatment and ***y*** is the duration of water leaching treatment in days

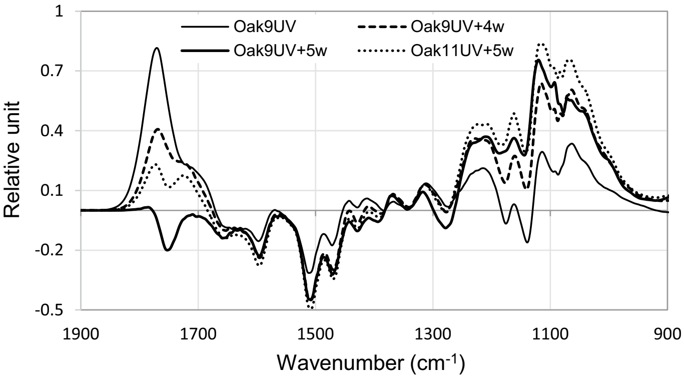

Fig. 4 Difference IR spectra of oak generated by UV radiation and water leaching. Legends: 9UV = 9-day UV treatment, ***x***UV + ***y***w, where ***x*** is the duration of UV treatment and ***y*** is the duration of water leaching treatment in days

treatment (1UV). The tick solid line represents the effect of 1-day water leaching (1UV + 1w), and the dotted line presents the effect of 2-day UV irradiation after the leaching (1UV + 1w + 2UV). The leaching hardly affected the lignin bands at 1505 and 1595 cm^{-1} wavenumbers. Alterations of these lignin bands will be discussed in detail later. 1-day water leaching reduced the absorption intensity of the unconjugated carbonyl groups at 1710 and 1763 cm^{-1} in different ways. The leaching by water removed almost the whole band at 1763 cm^{-1} but affected only slightly the band at 1710 cm^{-1}. The following 2-day UV irradiation (after the water leaching) generated a slightly greater absorption increase in the unconjugated carbonyl region than the 1-day UV irradiation at the beginning of the treatment.

A lifting effect is visible in the 1000–1200 cm^{-1} wavenumber interval in Fig. 2 when comparing Figs. 1 and 2. This effect is even more pronounced in Figs. 3, 4 and 5. However, this cannot be a real absorption increase in a broad wavenumber interval, which is because the Kubelka–Munk (*K–M*) equation does not provide the absorption spectrum properly if the surface roughness changes and the absorption is high enough. The *K–M* equation calculates the quotient of the absorption coefficient and the scattering coefficient. The shape of *K–M* function gives the absorption function properly if the light scattering remains constant during a treatment. However, photodegradation and water leaching increase the surface roughness (Tolvaj et al. 2014). The swelling lifts up the fibre edges during water leaching, and these fibres never return to the original position during drying. This phenomenon is also responsible for the change in surface roughness. Detailed discussion of this lifting phenomenon can be found in a previous work (Tolvaj et al. 2011). The history of the negative peak at 1092 cm^{-1} in Figs. 1, 2, 3, 4 and 5 shows properly the lifting effect. The well-visible negative peak at 1092 cm^{-1} in Fig. 1 is already a positive valley between two positive bands in Figs. 2, 3, 4 and 5. The large *K–M* value increase overlaps the real absorption changes, preventing the evaluation of the *K–M* spectrum in the 1000–1200 cm^{-1} wavenumber interval. This is the reason why the interpretation of this wavenumber region will be neglected during the further spectrum analysis.

The other species showed similar changes to beech after 1-day UV irradiation and water leaching. In the case of aspen, however, leaching reduced the absorption spectrum in the unconjugated carbonyl region where the original two bands were visible as a single band with a maximum at 1723 cm^{-1}. Another difference was that the lifting effect in the 1000–1200 cm^{-1} wavenumber interval was negligible for black locust species. Moreover, black locust was an exception during the whole test. The lifting effect for black locust was considerably smaller in all cases compared to the other investigated species (see Fig. 5 as well). The reason might be that black locust was the hardest species having extremely high extractive content. The lumens in black locust wood are filled with tyloses. The presence of tyloses reduces the roughness increase generated by the photodegradation.

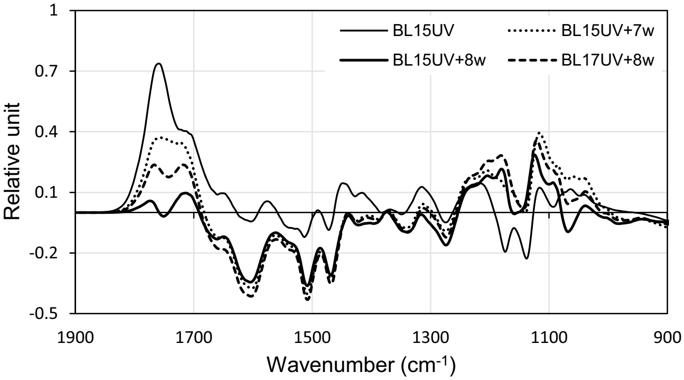

Fig. 5 Difference IR spectra of black locust (BL) generated by UV radiation and water leaching. Legends: 15UV = 15-day UV treatment, ***x***UV + ***y***w, where ***x*** is the duration of UV treatment and ***y*** is the duration of water leaching treatment in days

No significant difference was found between the effects of the 5-day pure UV treatment and the 5UV + 2w combined UV radiation and leaching treatment of aspen wood (Fig. 3). Only the band with the maximum at 1761 cm^{-1} was partly removed by the previous 2-days water leaching. The 2-days leaching did not affect the lignin bands at 1506 and 1593 cm^{-1}, and the intensity of the unconjugated carbonyls at 1721 cm^{-1} remained intact as well. The additional 1-day water leaching (5UV + 3w) reduced the absorption intensity of both unconjugated carbonyl bands considerably. The other examined species showed similar changes to aspen. Only for oak, a small negative band at 1745 cm^{-1} appeared. This alteration will be discussed later. An additional 2-day UV irradiation (7UV + 3w) generated only a little absorption increase in the unconjugated carbonyl region for aspen specimens. Absorption increase generated by this 2-day UV irradiation was a little greater for black locust and oak than for aspen. The previously discussed lifting effect is well visible in Fig. 3. Not only the leaching but the pure UV irradiation also produced lifting.

Continuing the treatments, the changes were prolonged. Figure 4 represents the effects of 9-day UV irradiation and 5-day water leaching in the case of oak wood. The degradation of both guaiacyl and syringyl lignin was considerably greater for leached samples than for non-leached samples during the 9-day UV treatments. The comparison basis is the "Oak9UV + 4w" spectrum in Fig. 4. The next 1-day water leaching (9UV + 5w) completely eliminated the absorption values in the whole unconjugated carbonyl region (1670 and 1820 cm^{-1}). A large absorption decrease appeared at 1745 cm^{-1} wavenumber. This negative absorption difference was also reported in previous works (Csanady et al. 2015; Bejo et al. 2019). The negative band shows that the water leached out molecules being originally in the wood independent of the applied treatments. Csanady et al. (2015) demonstrated that water leaching in total darkness produced the same absorption decrease at 1745 cm^{-1} wavenumber as the combined (UV + leaching) treatment. The negative band at 1745 cm^{-1} appeared first after 3-day leaching of oak. Comparing the investigated species, oak was the most sensitive species to leaching in the unconjugated carbonyl region. A small negative band appeared at 1650 cm^{-1} as well. This absorption decrease shows that water leached out water-soluble extractives. The same also happened with black locust after the third day of water leaching.

In contrast, black locust was the most stable species to water leaching. The negative band at 1745 cm^{-1} wavenumber appeared first after 8-day leaching (Fig. 5). Black locust samples showed the smallest lifting effect in the 1000–1200 cm^{-1} wavenumber interval. Moreover, the guaiacyl lignin in black locust suffered the smallest degradation during the pure UV irradiation among the investigated species. The high extractive content partly protects the lignin against the photodegradation, and the degradation products of lignin are relatively stable to water leaching. These results demonstrate that black locust is the most durable wood among the investigated species and therefore highly suitable for outdoor applications. There is a negative shift of the spectra in the 1440–1670 cm^{-1} wavenumber interval generated by leaching. This negative shift started with 1-day leaching and increased up to the 4th day of leaching, then stopped and remained steady during the investigated time interval. The shift in the 1540–1680 cm^{-1} wavenumber interval can be interpreted by the leaching of water-soluble extractives with conjugated double bond chemical systems. These extractives are responsible for the colour of wood. The reason of the negative shift in the 1440–1540 cm^{-1} wavenumber interval is unknown. Clarification of the reason of this phenomenon needs further investigations. The negative band with maximum at 1603 cm^{-1} is not a single absorption band of the syringyl lignin, which appears usually at 1595 cm^{-1}. It must be the superposition of two bands. The peak position of the other band is around 1610 cm^{-1}. None of the other investigated species presented this absorption decrease at 1610 cm^{-1}. Therefore, it is thought that one of the extractives of black locust is sensitive to photodegradation and the UV light degrades this molecule. Probably this extractive has an aromatic ring similar to syringyl lignin, because the absorption bands are close to each other.

There are differences among the investigated species regarding the time necessary for total leaching of the photodegradation generated unconjugated carbonyls. The two positive bands of unconjugated carbonyls disappeared after 5, 6 and 8 days of water leaching of oak, beech and aspen, respectively. The applied maximum 10-day leaching was not enough to diminish completely the two positive bands of unconjugated carbonyls in black locust. The band with a maximum at 1766 cm^{-1} disappeared, but the more stable band with a maximum at 1710 cm^{-1} remained as a small positive band even after 10-day water leaching of black locust.

Figures 1, 2, 3, 4, and 5 display the difference IR spectra in variably chosen situations during the applied 20-day treatments. The following figures show the absorption changes of individual bands throughout the whole treatment time. Relative absorption changes are presented, because the differences were calculated based on the normalised spectra to provide correct comparison. Figure 6 represents the absorption changes of oak at 1512 cm^{-1} wavenumber. This wavenumber belongs to the vibration of the aromatic ring in guaiacyl lignin. Negative values indicate the splitting of the aromatic ring caused by UV irradiation.

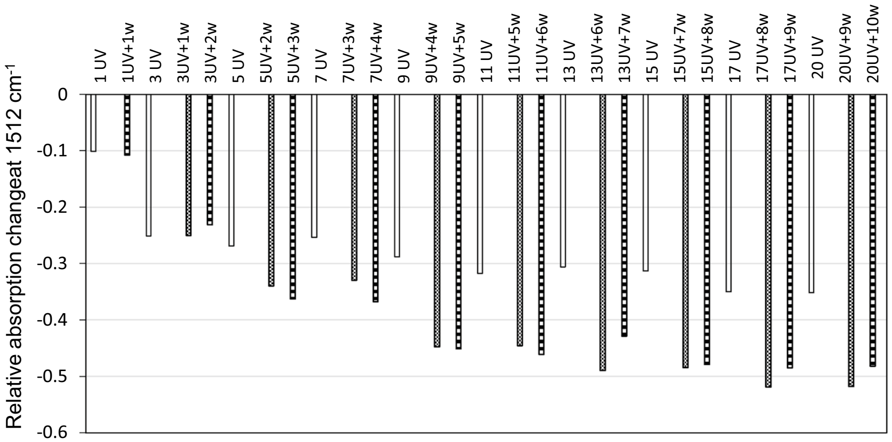

Fig. 6 Absorption band intensity change of guaiacyl lignin in oak at 1512 cm^{-1}. Empty columns represent the effect of pure UV treatment in dry condition. Legends: xUV = x-day UV treatment, xUV + yw, where x is the duration of UV treatment and y is the duration of water leaching treatment in days

In Fig. 6, the first empty column on the left represents the effect of 1-day UV irradiation, followed by the columns of repeated 1-day water leaching and 2-day UV irradiations. The degradation of lignin was intensive at the beginning of the treatments and the intensity of absorption decrease hardly changed after 11 days of UV irradiation for non-leached samples. After 5-day UV irradiation, leached samples suffered considerably greater lignin degradation compared to the samples getting only UV irradiation. The reason can be that water leaching further enables the UV radiation to degrade the aromatic rings of lignin in deeper layers of the samples. Beside oak, leached black locust samples suffered considerably greater lignin degradation compared to non-leached samples. These two species have high extractive content, and the extractives partly protected the lignin against the UV degradation. Leaching of extractives clearly reduced this protection. This phenomenon can be the second reason why the leached samples suffered greater lignin degradation than non-leached ones. In the case of aspen and beech, lignin degradation difference between leached and non-leached samples was small. This phenomenon can be explained by the low extractive content of aspen and beech.

The absorption change around 1600 cm^{-1} consists of the absorption region of syringyl lignin and that of conjugated carbonyl groups. Positive absorption increase is due to the generation of conjugated carbonyl groups as a result of the photodegradation of lignin and extractives. Degradation of syringyl lignin reduces the absorption in this wavenumber region. Figure 7 shows the absorption intensity change of syringyl lignin at 1595 cm^{-1} wavenumber. Positive values diminish the intensity of greater negative values during the photodegradation at 1595 cm^{-1} wavenumber. At the beginning of the treatments, lignin degradation was faster than the generation of conjugated carbonyl groups in non-leached samples (empty columns) up to the

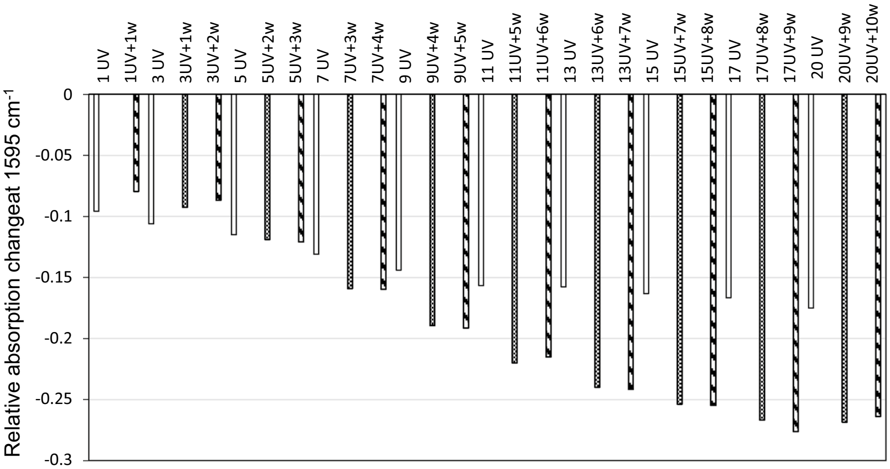

Fig. 7 Absorption band intensity change of syringyl lignin at 1595 cm^{-1} for aspen wood. Empty columns represent the effect of pure UV treatment in dry condition. Legends: xUV = x-day UV treatment, xUV + yw, where x is the duration of UV treatment and y is the duration of water leaching treatment in days

11th day of UV irradiation. After that, the trend changed; generation of conjugated carbonyls became more intensive reducing the growing intensity of the absorption decrease at 1595 cm^{-1}.

Water-leached samples suffered considerably greater lignin degradation than non-leached samples after 5-day UV irradiation. The reason might be that water leaching gives further access to UV radiation to degrade the aromatic rings of lignin in deeper layers of the samples. The other reason of the absorption decrease at 1595 cm^{-1} could be that water removes conjugated carbonyl groups being originally in the wood. In a previous work, colour measurement showed that the leaching partly removed both yellow and red chromophore molecules (Kannar et al. 2018). The other investigated species showed similar absorption change around 1595 cm^{-1} compared to aspen.

Absorption changes of unconjugated carbonyls of beech at 1713 cm^{-1} are presented in Fig. 8. The absorption change of these unconjugated carbonyl groups can be evaluated only for beech samples because this band is visible as a shoulder in the case of the other investigated species. Absorption change of non-leached samples (Fig. 8, empty columns) increased continuously during the whole investigated time interval. Leaching reduced the absorption intensity continuously. The absorption change values turned into negative values after 7-day water leaching. Negative values were generated by the leaching of carbonyl groups being originally in wood. UV irradiations after water leaching, (dotted columns in Fig. 8) generated new absorption increase in all cases.

Figure 9 represents the absorption change of unconjugated carbonyl groups in black locust samples absorbing at around 1766 cm^{-1}. Pure UV irradiation generated continuous absorption increase (Fig. 9, empty columns). The last two empty columns show a slight decrease, but it is because the real maximum shifted a

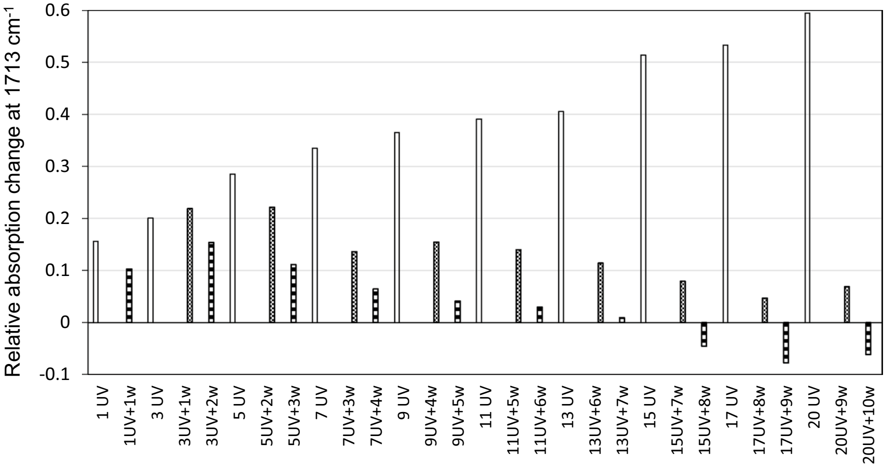

Fig. 8 Absorption band intensity change of the unconjugated carbonyls at 1713 cm^{-1} for beech wood. Empty columns represent the effect of pure UV treatment in dry condition. Legends: xUV = x-day UV treatment, xUV + yw, where x is the duration of UV treatment and y is the duration of water leaching treatment in days

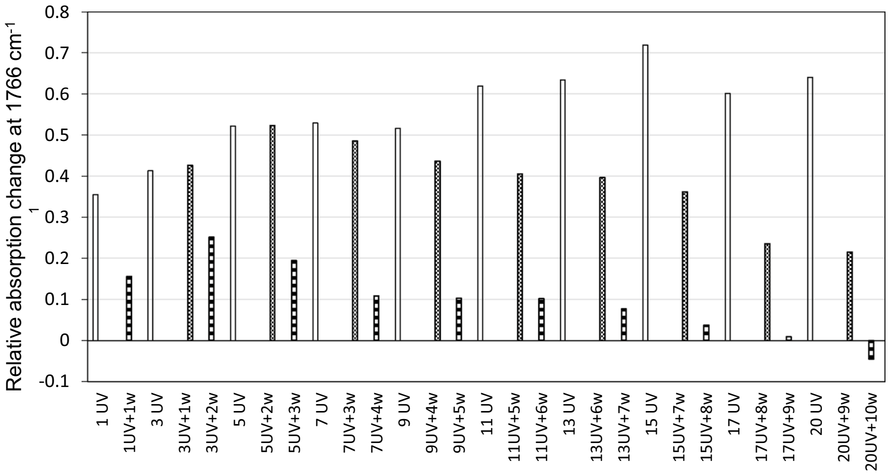

Fig. 9 Absorption band intensity change of the unconjugated carbonyls in black locust wood at 1766 cm^{-1}. Empty columns represent the effect of pure UV treatment in dry condition. Legends: xUV = x-day UV treatment, xUV + yw, where x is the duration of UV treatment and y is the duration of water leaching treatment in days

little towards smaller wavenumbers. Leaching reduced the absorption intensity continuously. The absorption change value turned into negative values generated by the tenth day of water leaching. Water leached out the absorption band around 1760 cm^{-1} of the other investigated species during shorter leaching time compared to black locust. This carbonyl band disappeared after 4-day leaching in the case of oak. The 2-day UV irradiation always increased the absorption intensity of leached samples at 1760 cm^{-1} considerably. This increase was similar to the absorption increase in non-leached samples up to the fifth day of UV irradiation. The absorption intensity of leached samples at 1760 cm^{-1} decreased after the fifth day of UV irradiation. This means that the photodegradation was unable to supply as many unconjugated carbonyl groups as were leached out by the previous water treatment.

Conclusion

Greater lignin degradation was found in the case of leached samples than in purely UV treated samples. The guaiacyl and the syringyl lignin showed similar degradation properties. Unconjugated carbonyl groups generated by the photodegradation proved to be the most sensitive chemical components to leaching. The photodegradation generated two absorption bands of unconjugated carbonyl groups at around 1710 and 1760 cm^{-1} wavenumbers. The band at 1760 cm^{-1} was much more sensitive to leaching by water than the band at 1710 cm^{-1}. Three to ten days of water leaching was enough to remove all unconjugated carbonyls generated by the photodegradation, depending on the species. The most sensitive species to water leaching was sessile oak. The most stable species for both photodegradation and water leaching was black locust.

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